



N77-28300

SEMI-ANNUAL REPORT

A FUNDAMENTAL APPROACH TO ADHESION:  
SYNTHESIS, SURFACE ANALYSIS,  
THERMODYNAMICS AND MECHANICS

by

David W. Dwight and James P. Wightman

Prepared for

National Aeronautics and Space Administration

July 1977

Grant NSG-1124

NASA-Langley Research Center  
Hampton, Virginia 23665  
Materials Division  
Donald J. Progar

Department of Chemistry  
Virginia Polytechnic Institute and State University  
Blacksburg, Virginia 24061

REPRODUCED BY  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U. S. DEPARTMENT OF COMMERCE  
SPRINGFIELD, VA. 22161

## NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

## TABLE OF CONTENTS

	<u>Page</u>
I. Introduction . . . . .	1
II. Experimental . . . . .	3
III. Results and Discussion . . . . .	5
IV. Conclusions . . . . .	32
V. Work Planned . . . . .	33
VI. Appendix . . . . .	34



## I. Introduction

The ability of SEM/EDAX to determine the physical and chemical composition of very small areas was used to study several, diverse types of samples representative of NASA-LaRC technology. More systematic investigation was carried out on two subjects in which earlier work had raised questions: (1) Differences in the results of grit-blasting Ti 6-4 adherends, and (2) The presence of extraneous elements--primarily silicon--in some polymer/HT-S fiber composites. Initial results were obtained from a fractured (ILS) Short-Beam Shear specimen, and from Ti 6-4 alloy, before and after a proprietary Boeing anodizing surface preparation for adhesive bonding. Photomicrographs and EDAX spectra were also obtained from new, fractured lap-shear strength specimens that employed PPQ and LARC-13 adhesives. These results substantially complete our basic data on the various combinations of adhesives and adherends.

During the current grant period, the DuPont 650 X-ray photoelectron spectrometer was installed and put into operation. Its design and operating characteristics differ considerably from the AEI ES100 apparatus previously employed. Thus duplicate runs were made on the polymers studied earlier. The results indicated the possibility of rapid, qualitative, polymer analysis, and the study was successfully extended to additional polymers and monomers. Some of these preliminary results were included in a manuscript prepared for publication in Polymer Preprints (see Appendix).

The experimental emphasis is shifting toward ascertaining the durability of surface treatments on titanium 6-4 and toughening mechanisms

for brittle polyimides. During the remainder of the grant period, we plan to characterize Ti 6-4 surfaces before and after four common surface preparations and also after exposure to conditions that effect an accelerated environmental exposure. Also planned are benchmark tests on toughening with epoxy systems where favorable results have been reported in the literature. Attempts will be made to apply similar technology to polyimides.

## II. Experimental

### A. Apparatus and Procedures

#### 1. Scanning Electron Microscopy/Energy Dispersive Analysis of X-rays (SEM/EDAX)

Photomicrographs were obtained using a polaroid camera back attached to the oscilloscope on the Advanced Metals Research Corporation Model 900 scanning electron microscope. Operating at 20 kV, high magnification views (500X-10,000X) gave information on the details of surface features, while survey scans at 20X-200X provided a check on the distribution of representative features that describe the surface. For convenience in studying the results, approximate vertical dimensions of each photomicrograph appear at the right in the figures, and the corresponding magnification is listed in each caption. Most specimens were cut to approximately 1 x 1 cm with either a high pressure cutting bar (titanium substrates) or a hack saw (composite substrates), and fastened to SEM mounting stubs with conductive, adhesive-coated, copper tape. Also a new punch-type sample cutter was constructed to obtain  $\frac{1}{4}$ -inch, circular samples required for the DuPont 650 ESCA spectrometer, and a few SEM specimens were prepared to determine whether this method changed surface structures. To enhance conductivity of insulating samples, a thin ( $\sim 200 \text{ \AA}$ ) film of Au/Pd alloy was vacuum-evaporated onto the samples. Photomicrographs were taken with the sample inclined  $70^\circ$  from the incident electron beam. Rapid, semi-quantitative elemental analyses were obtained with an EDAX International Model 707A energy-dispersive X-ray fluorescence analyzer attached to the AMR-900 SEM. A Polaroid photographic record of

each spectrum was made using a camera specially adapted for the EDAX oscilloscope output. Tracings of the spectra are juxtaposed in the figures to facilitate interpretation.

Cross-sections of composites were obtained by securing samples between rubber faces in a bench-top vice and driving a crack through the sample with one sharp blow of a hammer on a hand-held chisel.

## 2. Electron Spectroscopy for Chemical Analysis (ESCA)

Initial ESCA data were collected on an AEI ES-100 photoelectron spectrometer using an aluminum anode and digital data acquisition. A digital PDP-8e computer/plotter was used to deconvolute and display the spectra. Recently we repeated the experiments on a DuPont 650 photoelectron spectrometer with a magnesium anode and direct display of the spectra on a strip-chart recorder. This system provided analysis of polymer samples in minutes. This is, of course, a significant advantage for routine work even though computer analysis must be added later. We are working on more detailed comparisons but the qualitatively distinctive features of polymers are basically the same in both spectrometers.

### III. Results and Discussion

#### A. Scanning Electron Microscopy/Energy Dispersive Analysis of X-ray Fluorescence (SEM/EDAX)

##### 1. Titanium 6-4

##### a. Grit Blast Study

One set of samples of phosphate/fluoride treated Ti 6-4 analyzed by SEM/EDAX (Final Report, February 1977, Figures 7 and 8) showed numerous aluminum or aluminum oxide particles not observed previously. Lap Shear Strength testing with PPQ adhesive on these substrates gave low values, and our study of the fracture surfaces (Final Report, February 1977, Figures 9, 10, 11) also showed the particles, thus raising the possibility that the particles were a cause of low strength. We have repeated the analysis on another Ti 6-4 adherend taken from this set of samples. Several particles are seen at the lowest magnification in Figure 1, and EDAX analysis from these particles (Figure 8C) is positive for aluminum. Higher magnification photomicrographs in Figure 1 serve to characterize the microstructure typical of phosphate-fluoride treated Ti 6-4 as observed throughout the four years of our work.

In an attempt to determine the origin of the unexpected particles, three specially grit-blasted sets of Ti 6-4 coupons were prepared at NASA-LaRC to see whether residual aluminum oxide grit could be a factor. The microtopography of these samples is displayed in Figures 2-4; there is surprisingly little resemblance to the features in Figure 1. All of the specially prepared Grit Blast Study samples appear to be much more heavily

worked and fragmented than previous samples. (N.B. Visual inspection shows that the Grit Blast Study samples are much darker in the roughened areas than previous samples.) Furthermore, EDAX analysis (Figure 8B) was similar for all the Grit Blast Study samples, and indicated an unusually high aluminum content uniformly distributed, including fragments and substrata. The data point to the tentative conclusion that all of the Grit Blast Study specimens received a longer treatment than previous routine samples. This might result in the darkened appearance, the greater degree of micro-working of the surface, and an increased transfer of aluminum from the grit into the Ti 6-4 surface.

b. Boeing Anodized Surface Treatment

Photomicrographs of samples received from Boeing are seen in Figures 5-7. Immediately prior to the anodizing step, structures similar to previously observed Ti 6-4 "as received" are notable: white,  $\beta$ -phase flakes embedded in a cratered, amorphous, grey  $\alpha$ -phase alloy (Figure 5). After anodizing the oxide layer appears with many, very irregular pits, as observed in the sample obtained last year from NASA LaRC (see Final Report, February 1977, Figure 6). However, the dense population of small ( $< 0.5\mu\text{m}$ ) nodules is absent from the new samples. The effect of the new, punch-type sample cutter is negligible, judging by the fact that Figures 6 and 7 are virtually identical and the former sample was cut with tin snips. Close inspection of the 10,000X view in Figure 7 gives the impression that the anodized oxide layer is rather low-density and uniformly porous at the level of 1000 Angstrom units or less. EDAX gave identical results (Figure 8A) before and after anodizing, and there is a

basic correlation also with previous results on "as received" or normal surface treatments (Final Report, February 1977, Figure 3).

## 2. HT-S Graphite Fiber/Polymer Composites

Previously we had used EDAX only occasionally on composite substrate samples. Usually the data showed only the Au/Pd coating: the lighter elements (below fluorine) are not detected by X-ray fluorescence. Occasionally, however, some extraneous element would appear. Now we have systematically examined cross-sections of HT-S graphite fiber composites with matrix polymers P13N, Skybond 710, NR-150B2 and PPQ. Generally, the presence of extraneous elements, such as our conjecture of silicon from mold release agents, has been ruled out. Rarely was any element detected, and never in a uniform concentration over any appreciable area, as would be expected in the case of diffusion of contamination.

There were a few instances where several extraneous elements were concentrated in small, isolated areas that could be described as chunks of debris resulting from fracture when the samples were split with the chisel. Two examples are shown in Figure 9 and the EDAX results in Figure 10. In the center of the top photomicrograph in Figure 9 is an accumulation of chunks of debris, apparently matrix resin and Al, Si, Cl, K, Ca, Fe, Cu and Zn were found uniformly distributed throughout. No elements were found in either the graphite rods or the smooth matrix polymer areas adjacent to the debris. The same elements were found isolated in the lower right tip of the relatively large particle shown in the bottom of Figure 9. Perhaps small amounts of salts, catalysts or other ionic constituents of polymerization recipes all concentrate during drying

and cure into tiny, isolated regions. In any case, their occurrence is rare and their influence probably minor.

Photomicrographs of a tested Inter-Lamellar (Short Beam) Shear specimen are shown in Figure 11. The nature of the failure is more easily observed in the split cross-section at the bottom of the figure. This was the first such sample studied with the "scouting" objective to see whether any distinctive features could be determined on these small, difficult-to-handle specimens. More samples with different strength values would need to be examined to find whether SEM could be predictive or diagnostic for strength.

### 3. Fracture Surfaces

#### a. PPQ

Figure 12 shows representative features of a LSS sample prepared with Ti 6-4 anodized adherends and PPQ adhesive on scrim cloth. Low strength resulted after the joint was left for three days in boiling water and then tested at 550<sup>0</sup> F. Failure was 90% "near-interfacial", as indicated on the left. The adhesive fractured vertically, leaving part on each adherend, and the "bare" areas are covered with thin flakes of primer that were drawn in the direction of stress. This ductile fracture is also seen in areas of bulk adhesive failure on the right.

Representative views of two samples with anodized Ti 6-4 coupons as one adherend and composites (one with Skybond 710 matrix and the other with NR-150B2) as the other adherend, and PPQ (unsupported) adhesive are shown in Figure 13. Both samples gave moderate strength when tested at room temperature. The Skybond 710 sample had a three day water boil, and showed about 60% failure in the composite surface, 40% titanium interfacial, while the NR-150B2 showed > 80% failure at the titanium surface.



In both instances, black "smudges" seen in the upper left photomicrograph appeared on the titanium surfaces. Higher magnification views of these anomalous, dark areas are shown in Figure 14, where they have features distinctive of corrosion pits. Indeed, EDAX analysis (Figure 15) shows that the crystal-like growths projecting up from the dark background are composed of sodium and potassium chloride.

b. LARC-13/Ti 6-4

Figures 16-19 are rather similar, in keeping with the similarity in lap shear strength values. Interfacial failure and voids are the predominant features. Also, the adhesive-side of the interfacial failure replicates the adherend poorly, further indicating low flow that probably contributed to void formation. The sample aged and tested at 600°F had the greatest proportion of bulk failure.

Considerably higher strength was obtained with the samples shown in Figures 20 and 21, and interfacial failure was decreased proportionally. Perhaps there was better flow due to a difference in formulation: the color of the "flash" was distinctly lighter, and even the adherends were lighter. The void content was quite similar however. The high filler content in the latter sample appeared to effect greater bulk fracture, thus improving strength.

B. Electron Spectroscopy for Chemical Analysis (ESCA)

Fundamental studies correlating polymer structure (or more correctly, organic functional groups) with ESCA spectra are needed to firmly establish the technique and provide background information for applications of ESCA to practical applications where compositions are unknown. The installation

of the DuPont 650 Photoelectron spectrometer has greatly facilitated our efforts in this area because spectra are obtained rapidly and displayed directly. This has allowed us to repeat much of the work done last year on the AEI ES-100, and to examine the important, distinctive details such as side-bands and satellite structures.

Spectra have been collected from a wide variety of engineering polymers and copolymers, and many monomers also. Most of the samples do not contain functionality that produce large chemical shifts that facilitate interpretation of ESCA spectra in fluoropolymers or inorganic compounds. Nevertheless, qualitative identification can be effected by careful inspection of the peak shapes, positions and intensities, and satellite structures.

Reduction of the ESCA data into publishable form is time-consuming and still an area of research. For example, deconvolution of overlapping peaks and quantitative ratios of peak areas must eventually become standard procedure. Our spectra from PPQ, LARC-13, and several polyimide monomers for example, need this data treatment to facilitate interpretation.

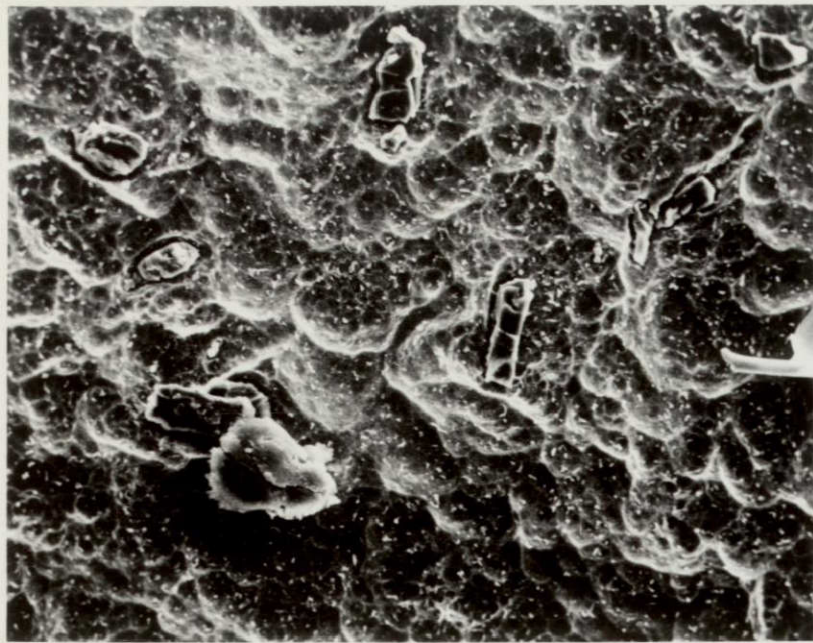
The use of a pantograph to reduce the peak sizes so that they can be juxtaposed easily was effective to show some of the potential of ESCA analysis of polymers in cases where distinctive features were clear without deconvolution or quantitative analysis of peak areas. Our initial results in this area have been submitted for publication in Polymer Preprints; a copy of this manuscript is contained in the Appendix. This paper will be presented at the ACS National meeting in Chicago, and an expanded version published in the Advances in Chemistry series. Also we are working on another paper for presentation in October at the regional ACS meeting in Charleston, West Virginia.

FIGURE 1.

Four magnifications (500X, 2000X, 5000X, 10,000X) of  
phosphate/fluoride treated Ti 6-4 samples of 10/76 origin.

Particles are suspected to be grit blast residue;

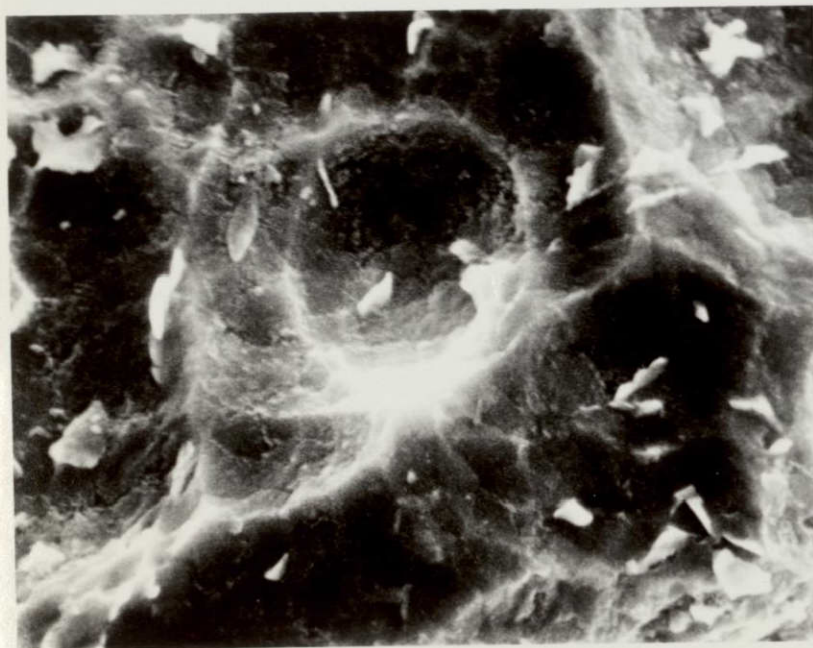
EDAX analysis shows aluminum (Figure 8C).



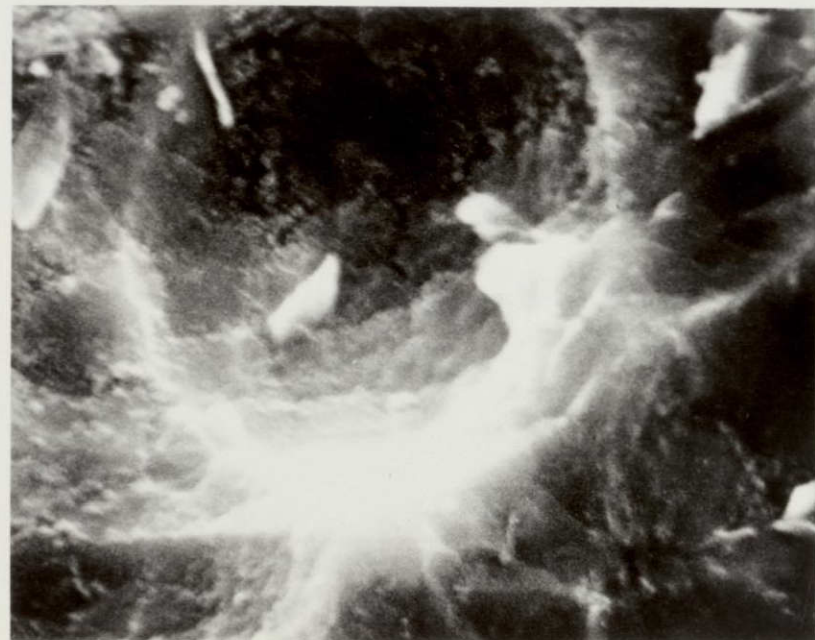
0.2mm



50  $\mu$ m



20  $\mu$ m



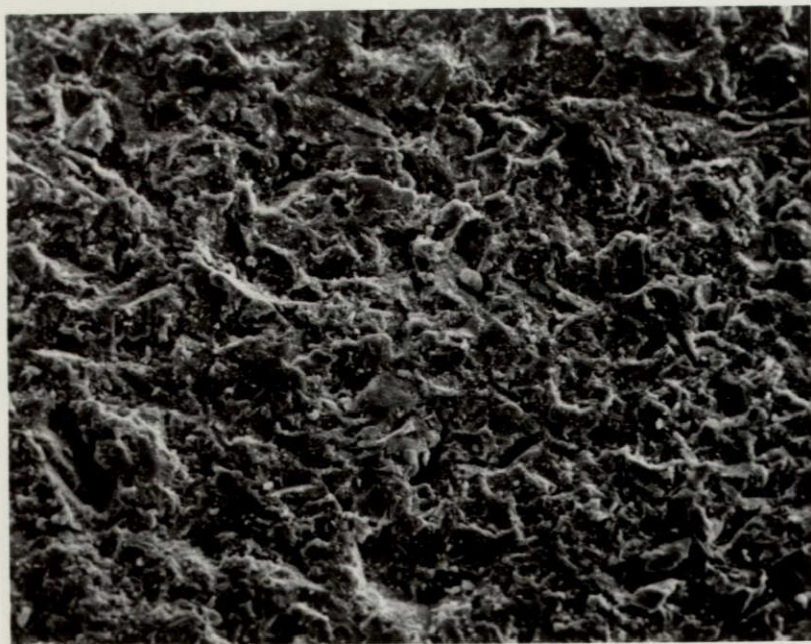
10  $\mu$ m

11-9

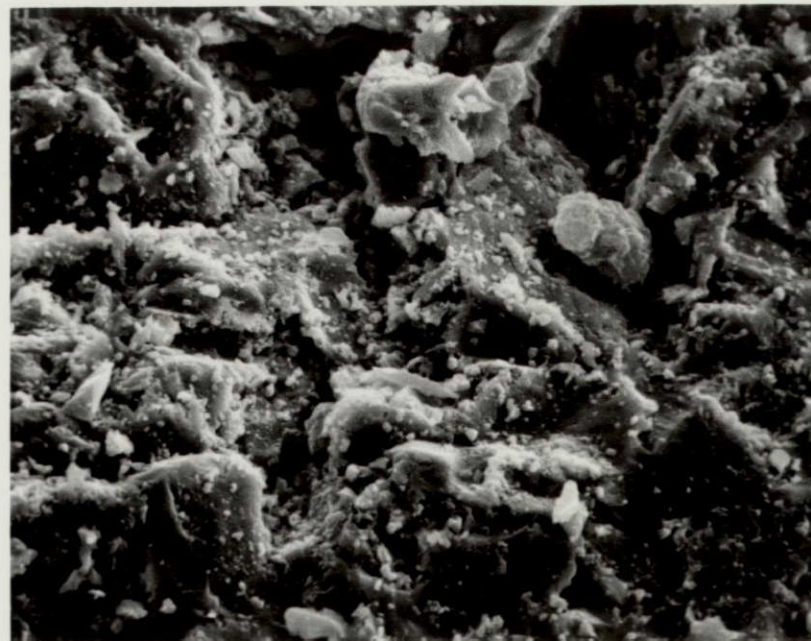


FIGURE 2.

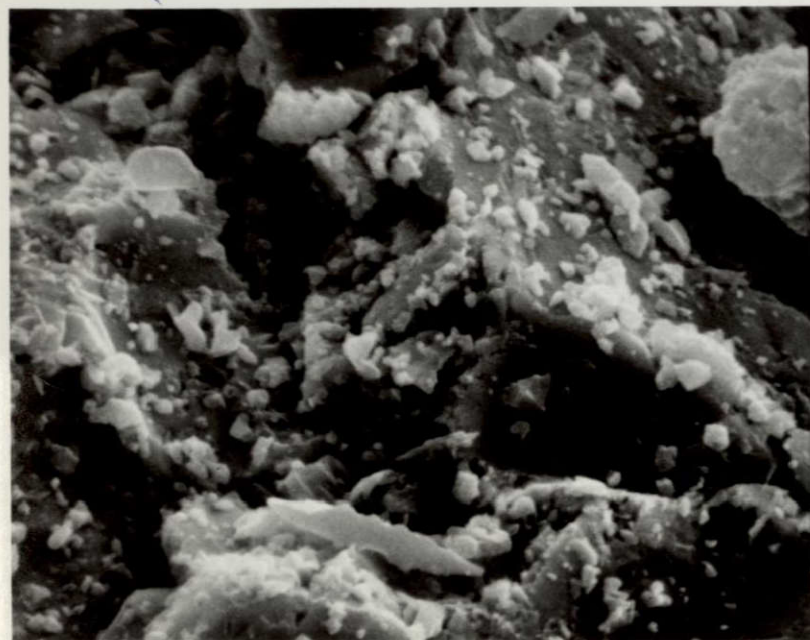
Four magnifications (500X, 2000X, 5000X, 10,000X) of Grit  
Blast Study Sample hand blasted (80 psi, 120 grit) in  
Bldg. 1 NASA-LaRC. Freon cleaned. Heavily worked,  
fragmented remains of previous Ti 6-4 sample.  
Fracture debris,  $0.1\mu\text{m} < d < 10\mu\text{m}$ , densely scattered.  
Excess aluminum content is shown by EDAX (Figure 8B).



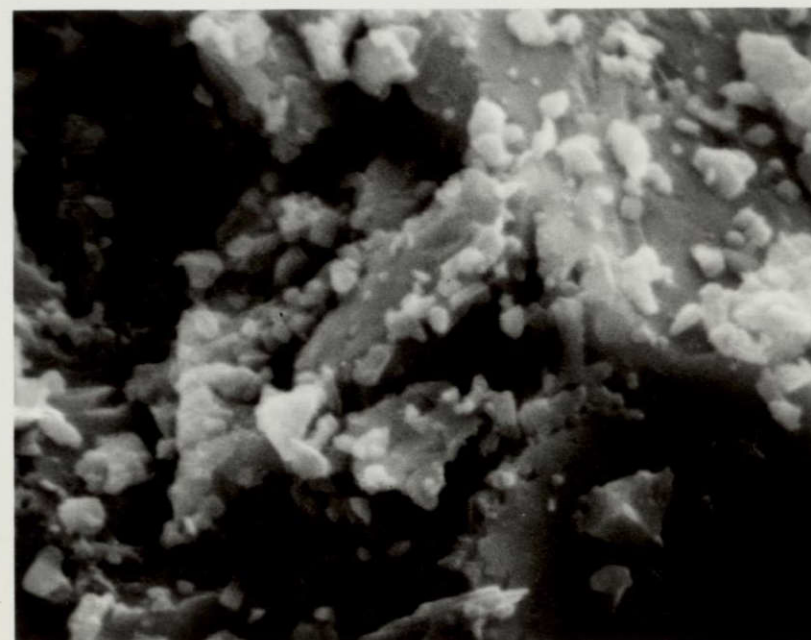
0.2 mm



50 μm



20 μm



10 μm

17-a





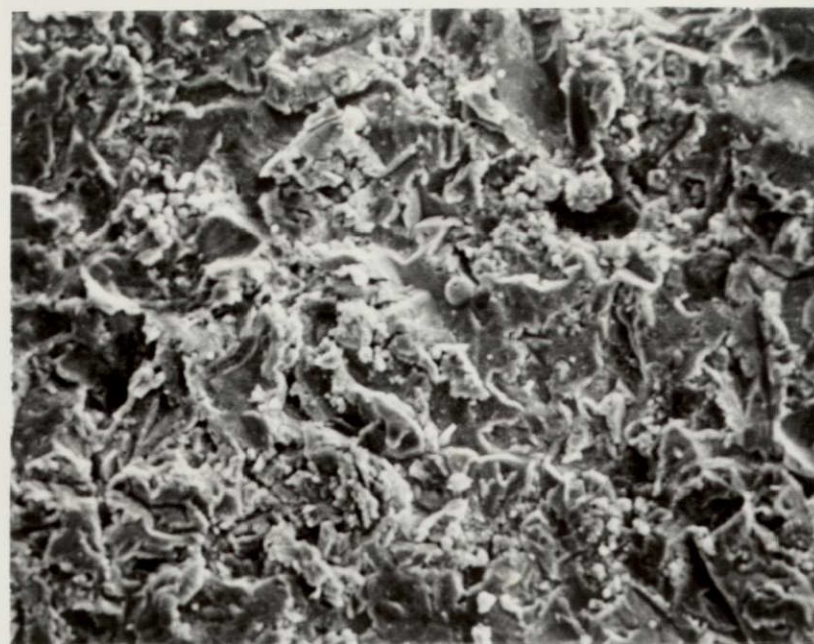
FIGURE 3.

Four magnifications (200X, 500X, 2000X, 5000X) of one of six grit blasted whole panels "All done in MP and DS (Freon cleaned) Lee Bryant." Fewer particles and possibly different micro-working than previous sample; EDAX identical-even the 5 $\mu$ m sphere.



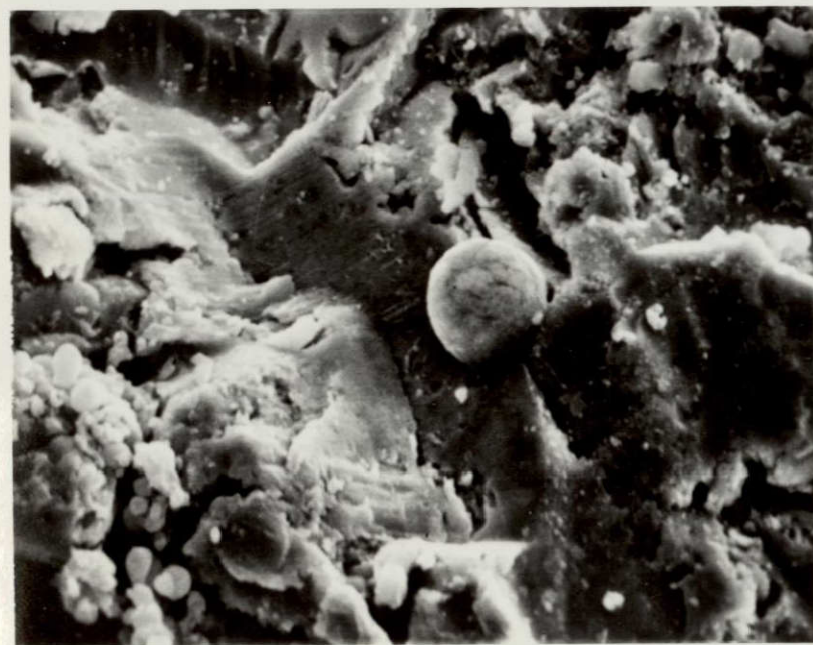


0.5mm



0.2mm

13-a



50  $\mu$ m



20  $\mu$ m

ORIGINAL FROM  
OF THE  
OF THE



FIGURE 4.

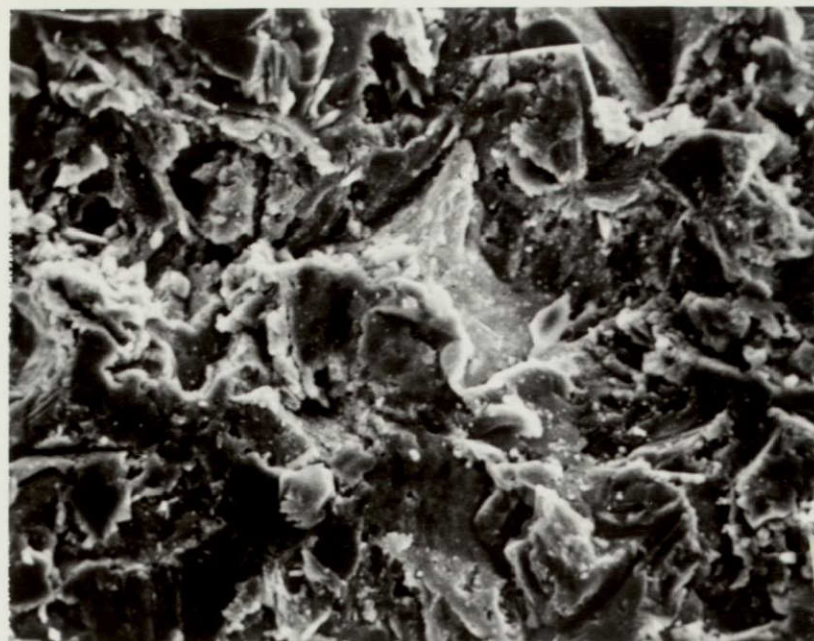
Top. Two magnifications (200X, 1000X) of Grit Blast Study sample; machine blast (MP and DS shop) perpendicular, 6"-8" from surface, 120 Al<sub>2</sub>O<sub>3</sub> grit, 80 psi pressure. Not Freon cleaned.

Bottom. Two magnifications (200X, 1000X) of same sample shown in Figure 2.





0.5mm



100  $\mu$ m

ORIGINAL PHOTO  
OF PORE QUALITY

14-a



0.5mm



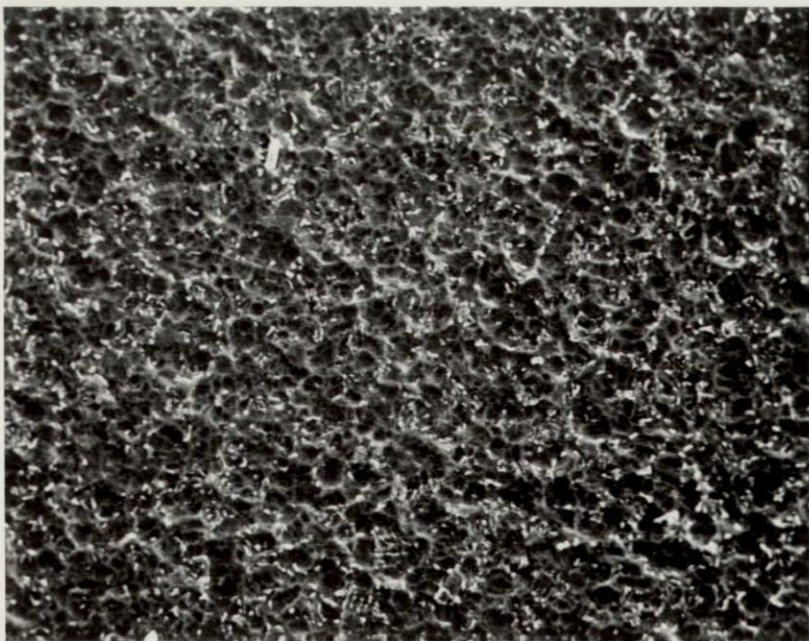
100  $\mu$ m



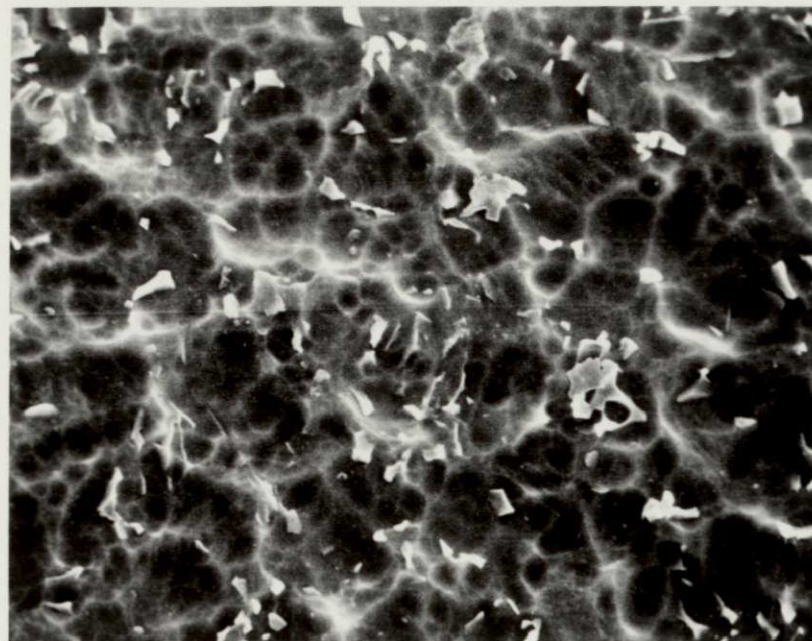
FIGURE 5.

Four magnifications (500X, 2000X, 5000X, 10,000X) of  
Boeing Ti 6-4 sample prior to anodizing step.



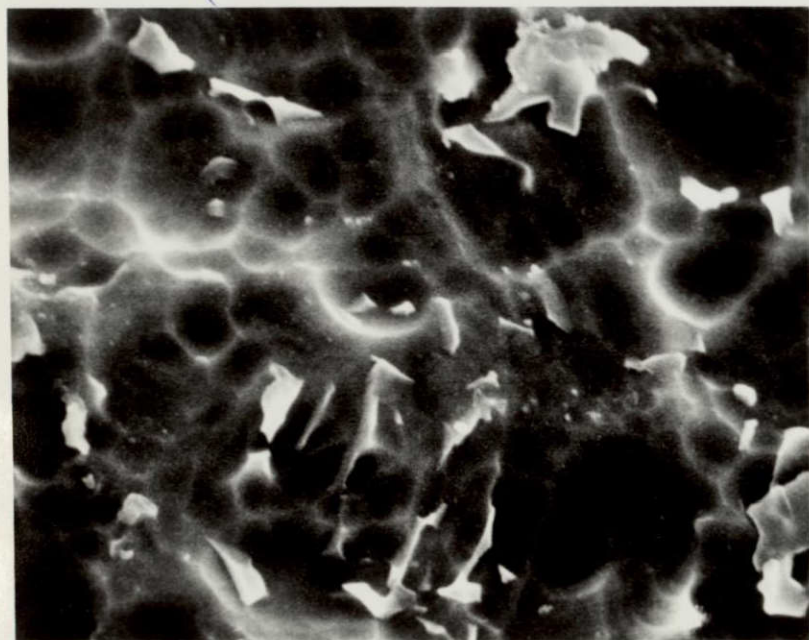


0.2mm

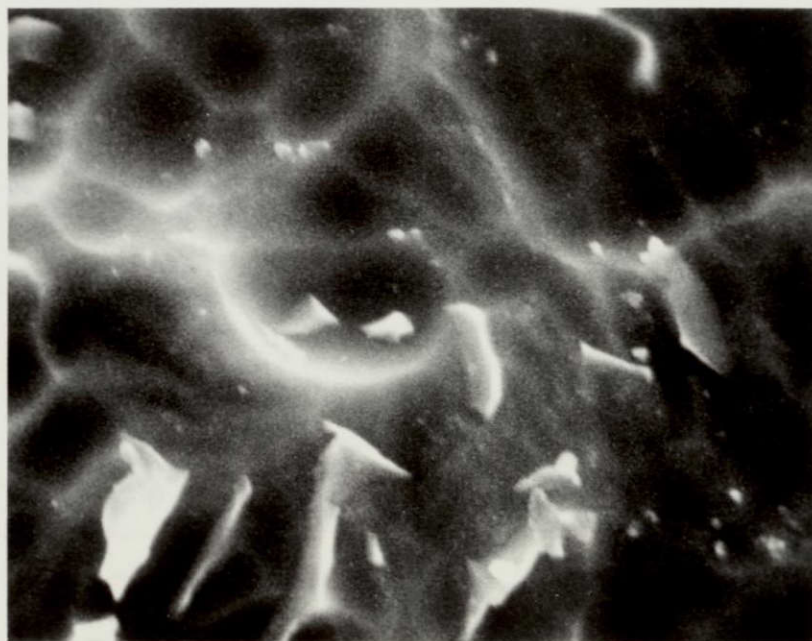


50  $\mu$ m

ORIGINAL IMAGE  
AP POOR QUALITY



20  $\mu$ m



10  $\mu$ m

15-a

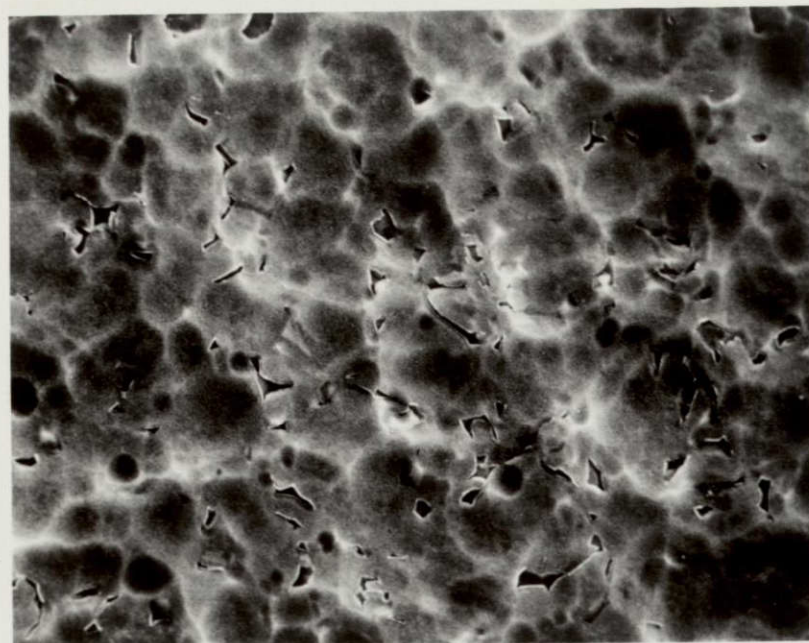


FIGURE 6.

Four magnifications (500X, 2000X, 5000X, 10,000X) of  
Boeing Ti 6-4 anodized sample.  
Cut with tin snips.

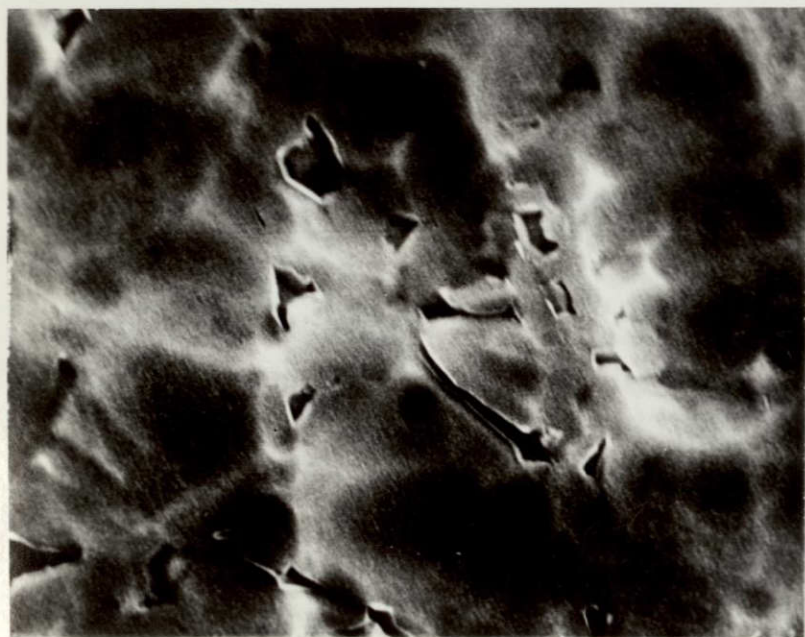


0.2mm



50  $\mu\text{m}$

16-a



20  $\mu\text{m}$



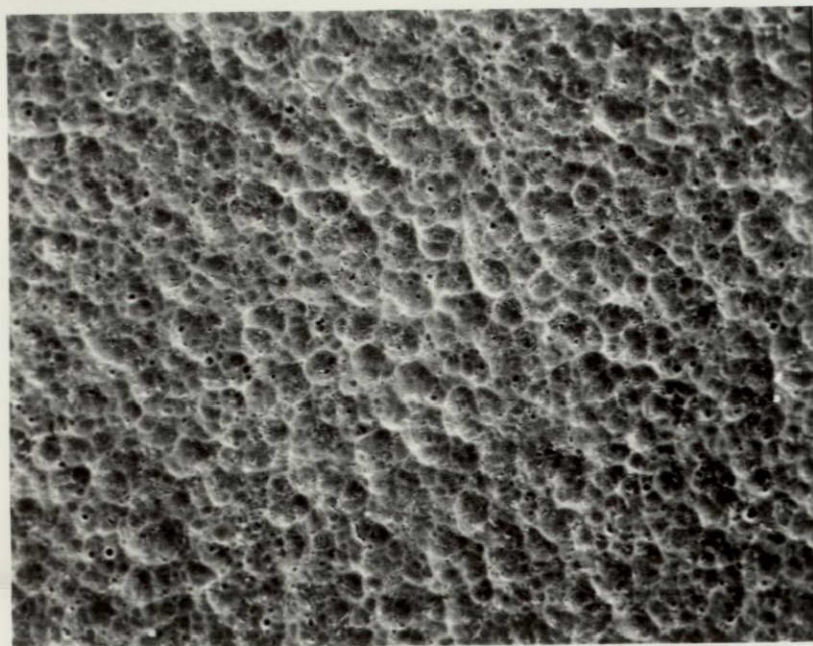
10  $\mu\text{m}$



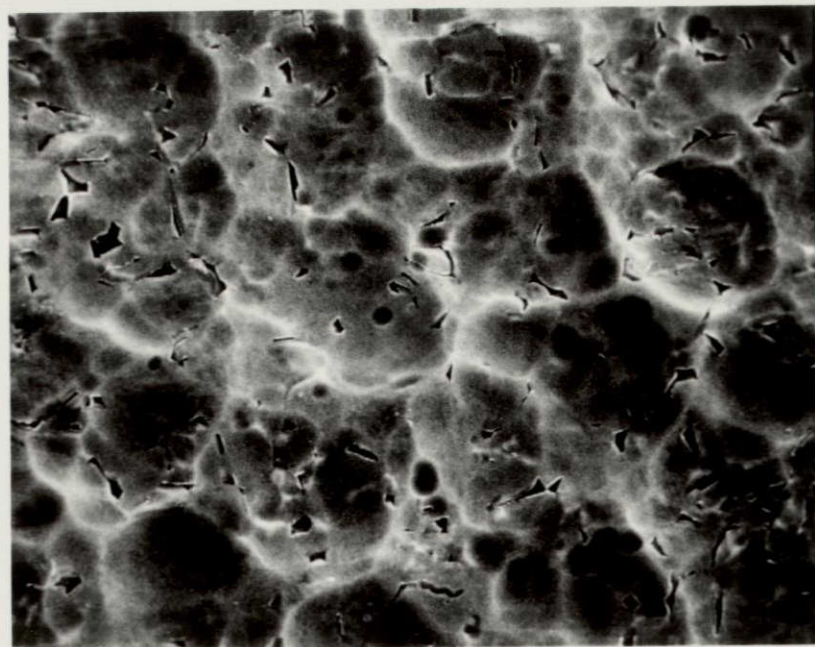
FIGURE 7.

Four magnifications (500X, 2000X, 5000X, 10,000X) of  
Boeing Ti 6-4 anodized sample. Cut with punch for  
DuPont 650 ESCA samples, micropores,  $d < 500 \text{ \AA}$ .



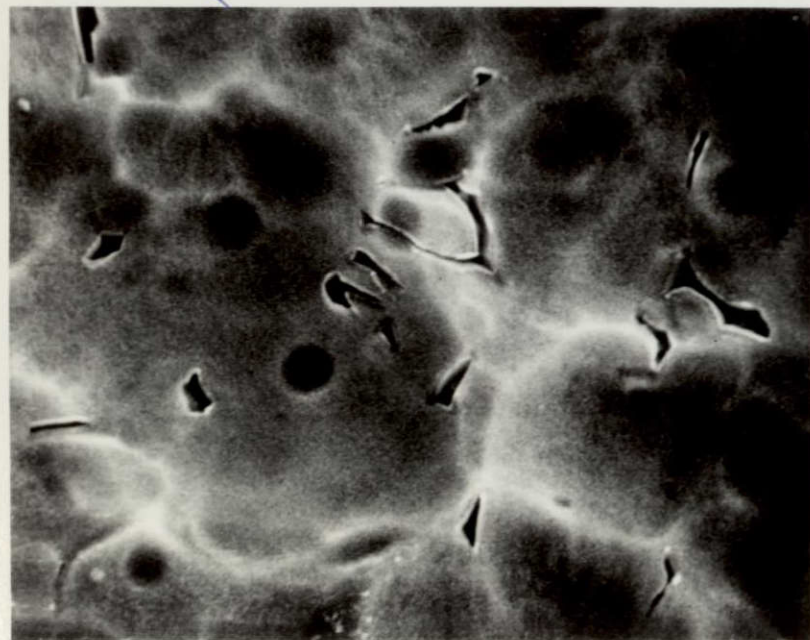


0.2mm

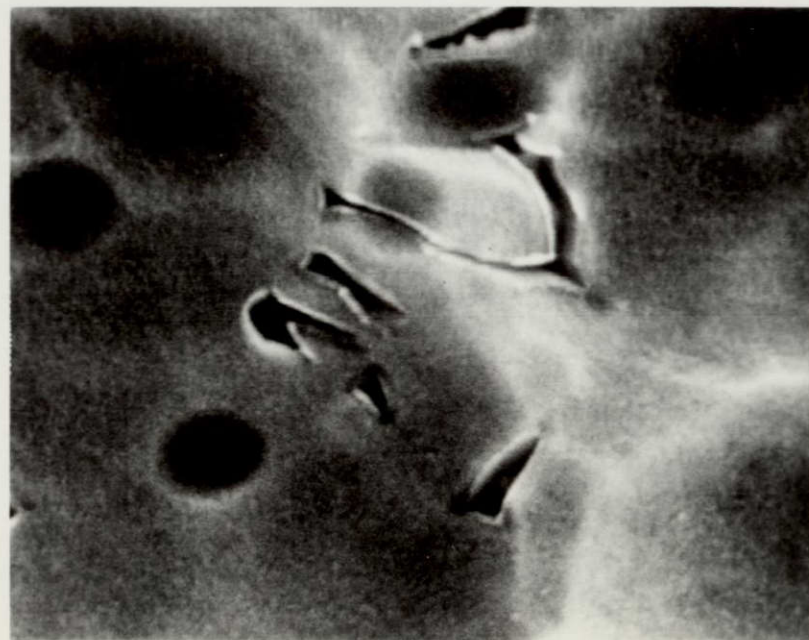


50  $\mu\text{m}$

17-a



20  $\mu\text{m}$



10  $\mu\text{m}$

OF Pore Structure



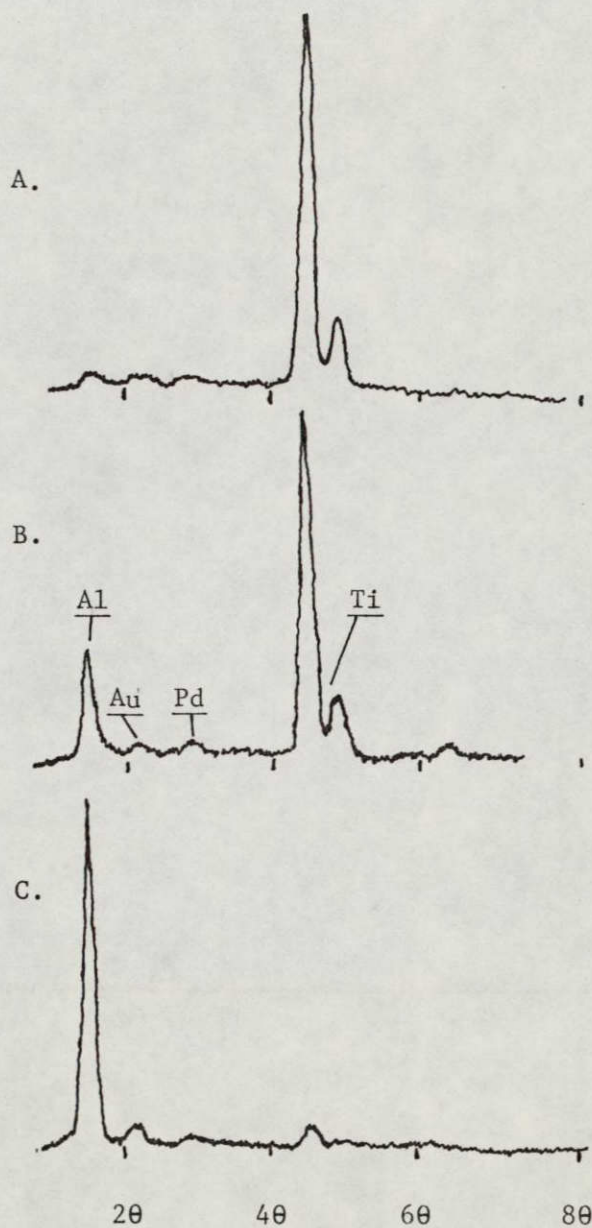


Figure 8. EDAX spectra typical of A. Ti 6-4 as received or after normal surface preparations. B. Ti 6-4 after "special" grit blast. C. Particles found on samples received 10/76; identical analysis for Al powder filler.

FIGURE 9.

Two magnifications (2 @ 2000X, 10,000X) of a split cross-section of previous sample. Areas with particulate debris have concentrations of Al, Si, Cl, K, Ca, Fe, Cu and Zn as shown in the EDAX spectrum in Figure 10.



19-a



50 μm



50 μm



10 μm

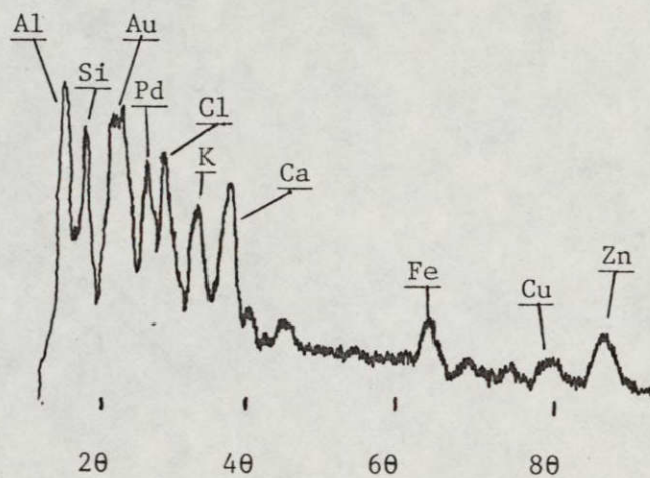


Figure 10. EDAX spectrum taken from the debris particle in Figure 9.



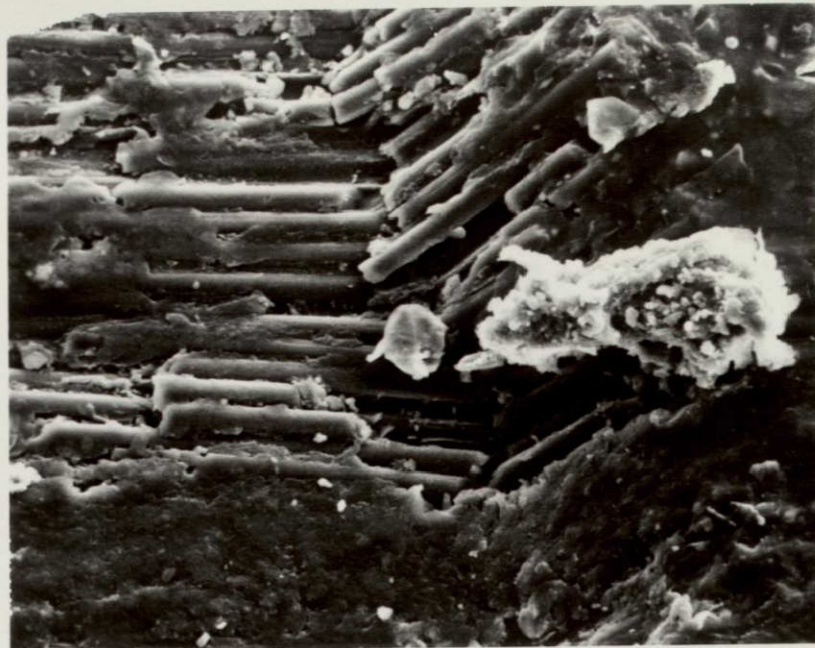
FIGURE 11.

Two magnifications (200X, 500X) of outside (Top) and inside (Bottom) of a PPQ (1:3) SRI2 Inter-Lamellar Shear specimen tested at 550°F = 5200 psi.





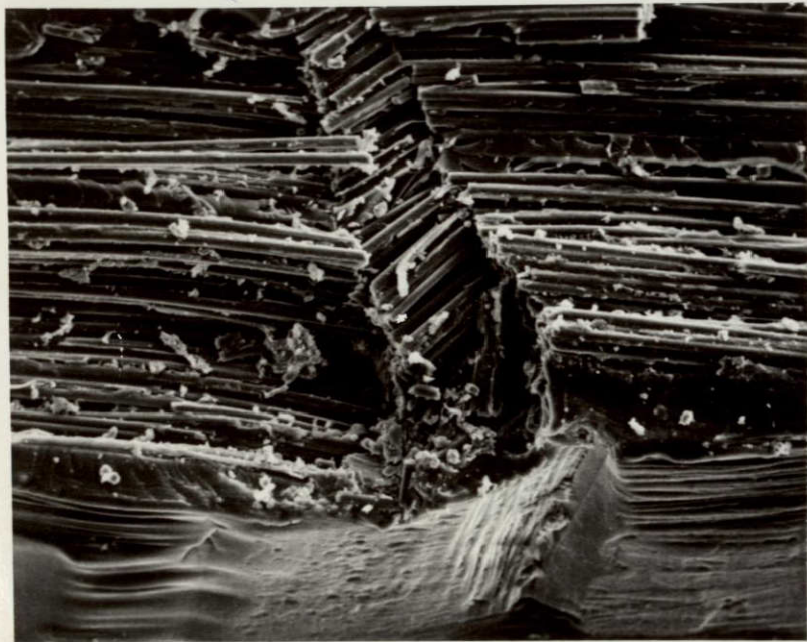
0.5mm



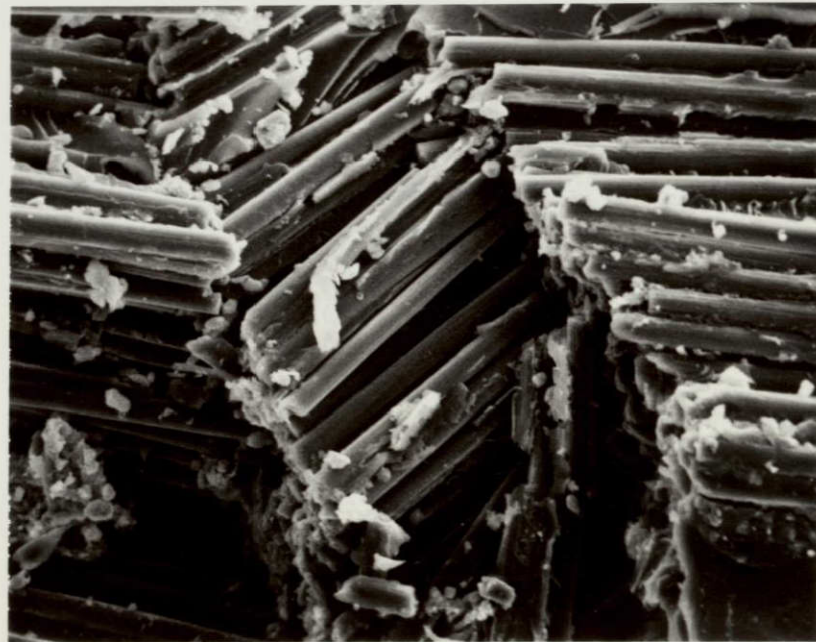
0.2mm

ORIGINAL PAGE IS  
OF POOR QUALITY

h/a



0.5mm



0.2mm



FIGURE 12.

Four magnifications (20X, 50X, 200X, 500X) of fracture surface of PPQ 413 (on scrim cloth)/Ti (anodized) joint tested at 550°F after 3 days water boil - 710 psi. Ductile fracture in adhesive, fiber/adhesive interfacial failure, primer/adherend "interfacial" failure, having thin flakes of primer adhering.

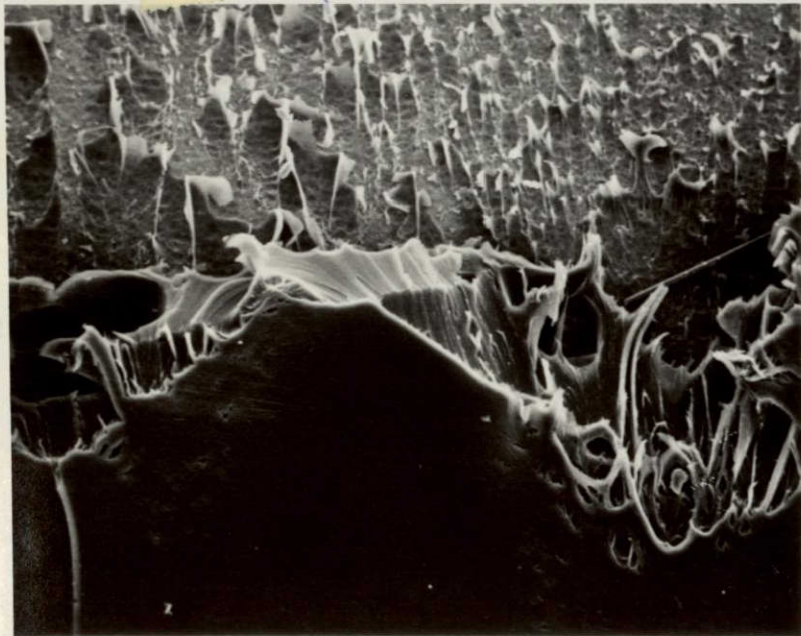




5mm



0.2mm



0.5mm



0.2mm

193-

202

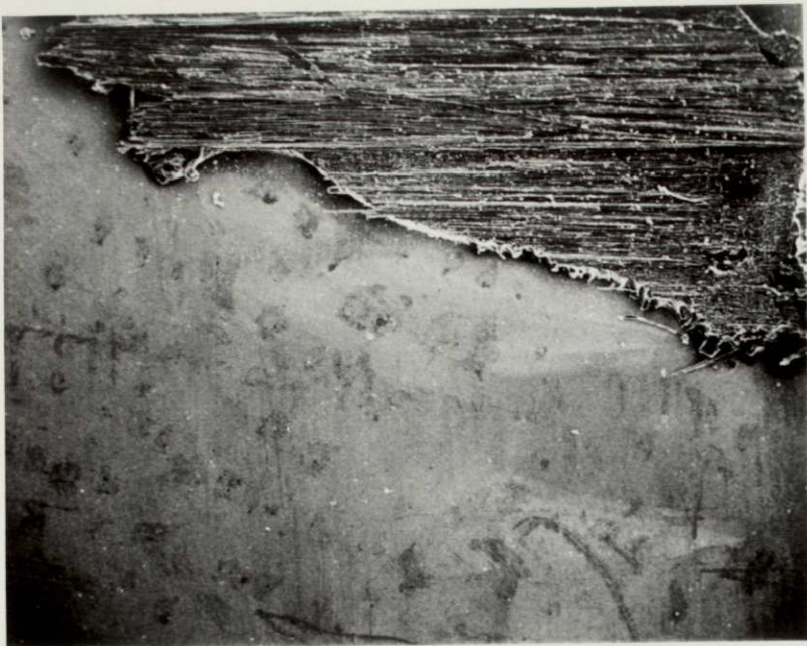
193-



FIGURE 13.

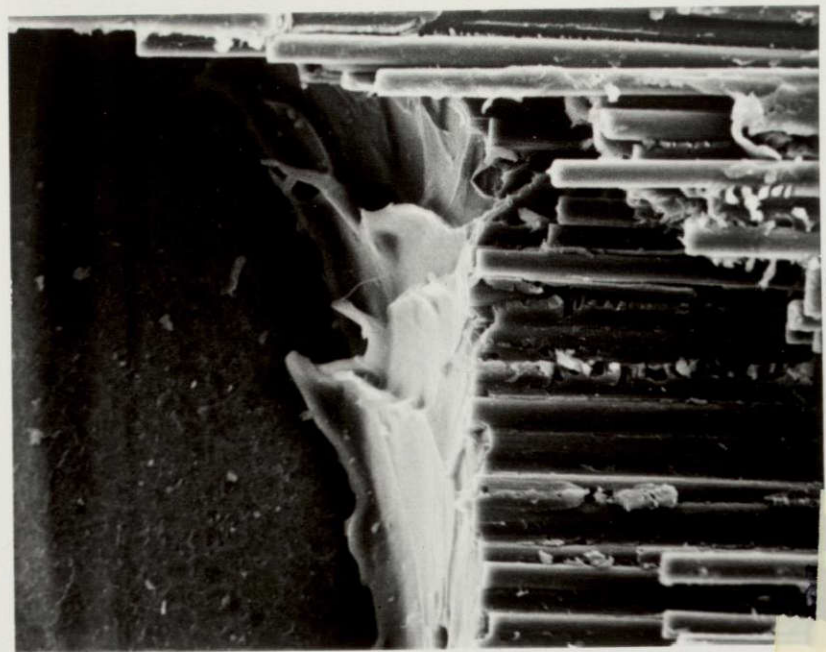
Three magnifications (20X, 500X, 1000X) of PPQ 413/Ti (anodized)/NR-150B2-HTS composite joint tested at room temperature = 2400 psi. (Bottom Left) one magnification (500X) of PPQ 413/Ti (anodized)/Skybond 710-HTS composite tested at room temperature after three days water boil = 2750 psi. Both samples very similar. Ti surface has numerous dark "smudges" that are seen to be salt pits in the next two figures.



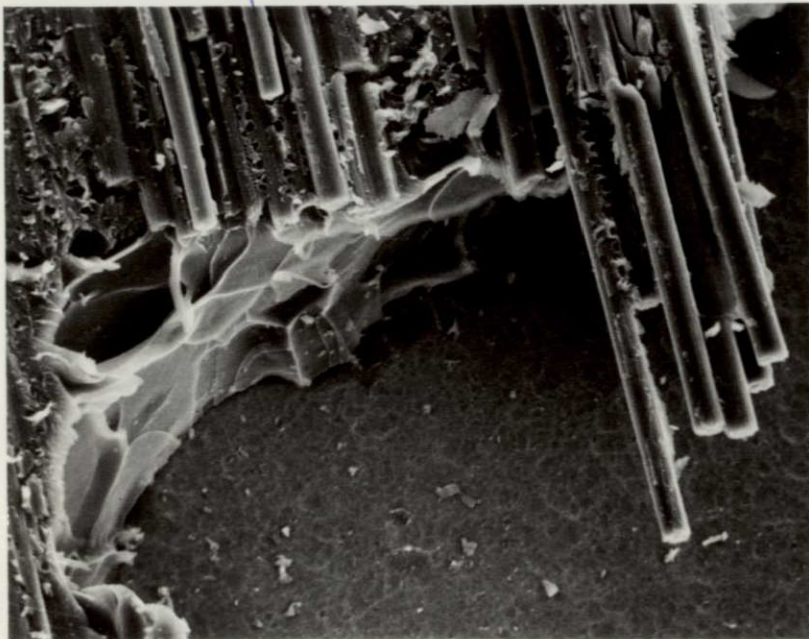


5mm

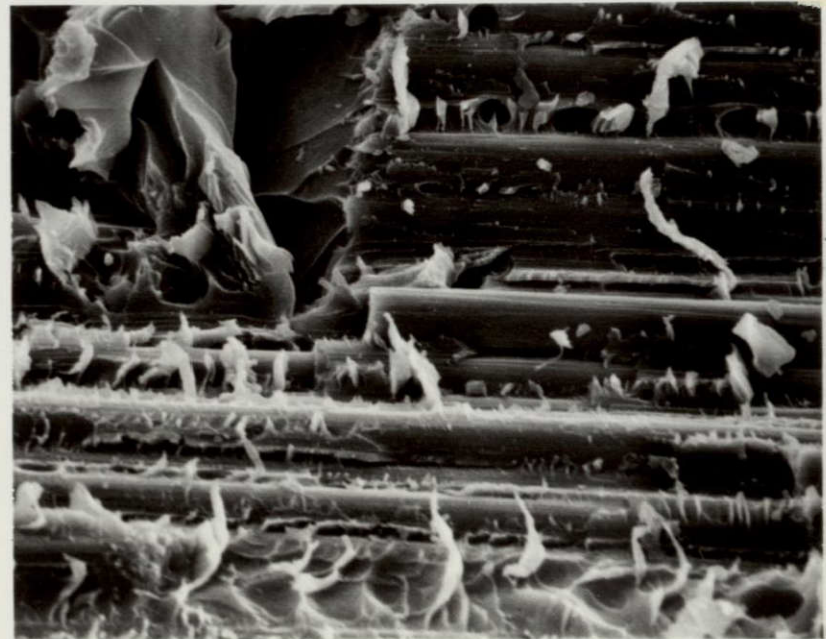
93-a



0.2mm



0.2mm



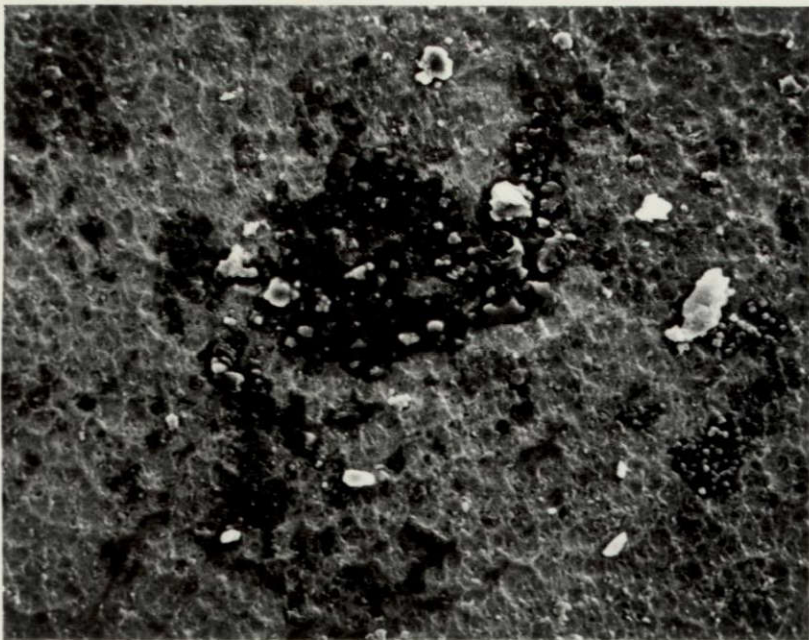
100 μm



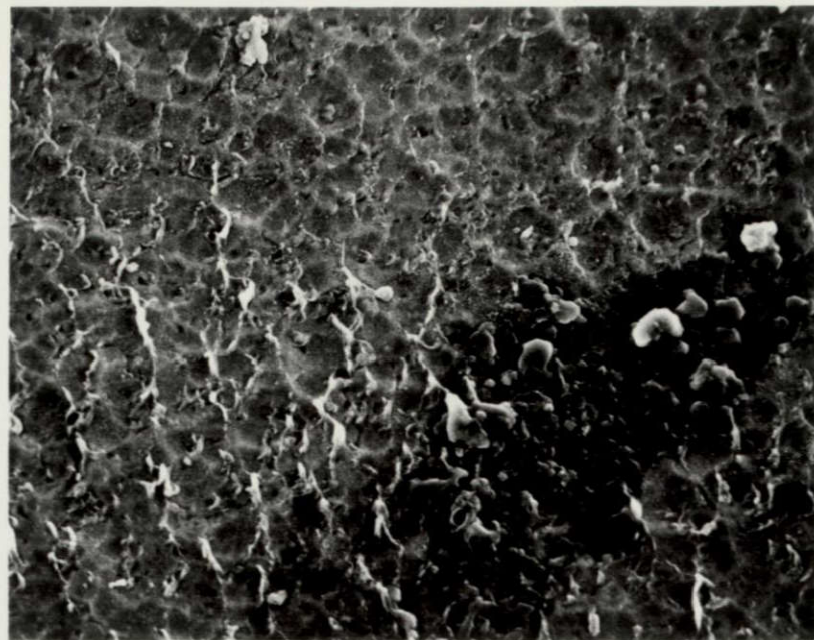
FIGURE 14.

Three magnifications (500X, 2 @ 1000X, 2000X) of adherend areas from the previous two samples. These features look like corrosion pits and EDAX (Figure 15) shows the crystals to be sodium and potassium chloride.



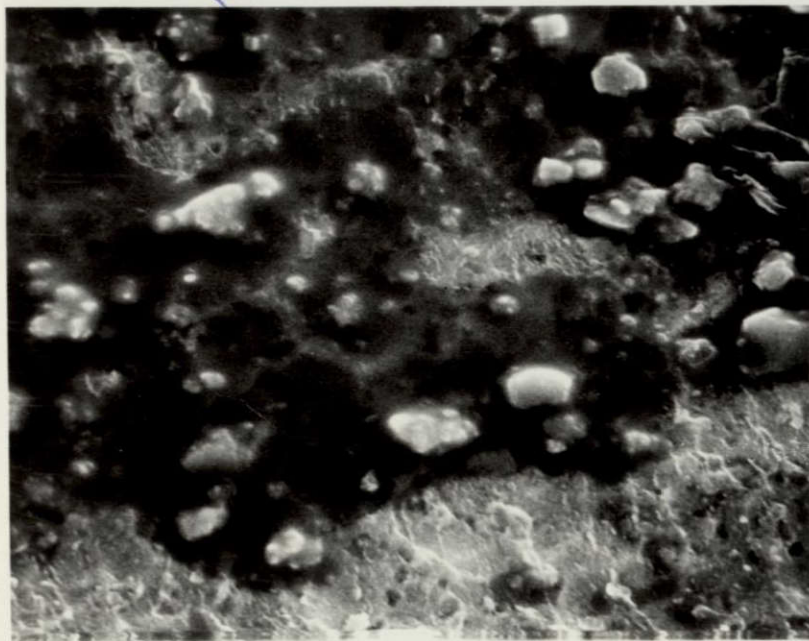


0.2mm

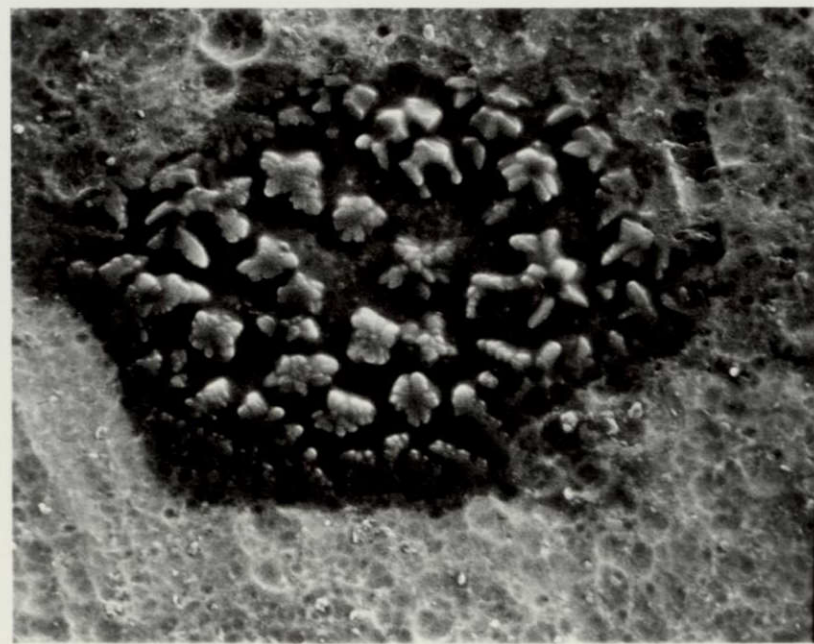


100 μm

74a



50 μm



100 μm

ORIGINAL PAGE IS  
OF MICROFILMED



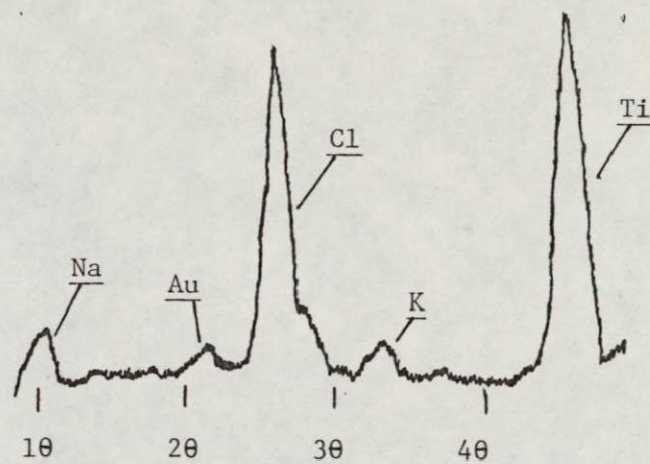


Figure 15. EDAX spectrum taken from corrosion pit in Figure 14.

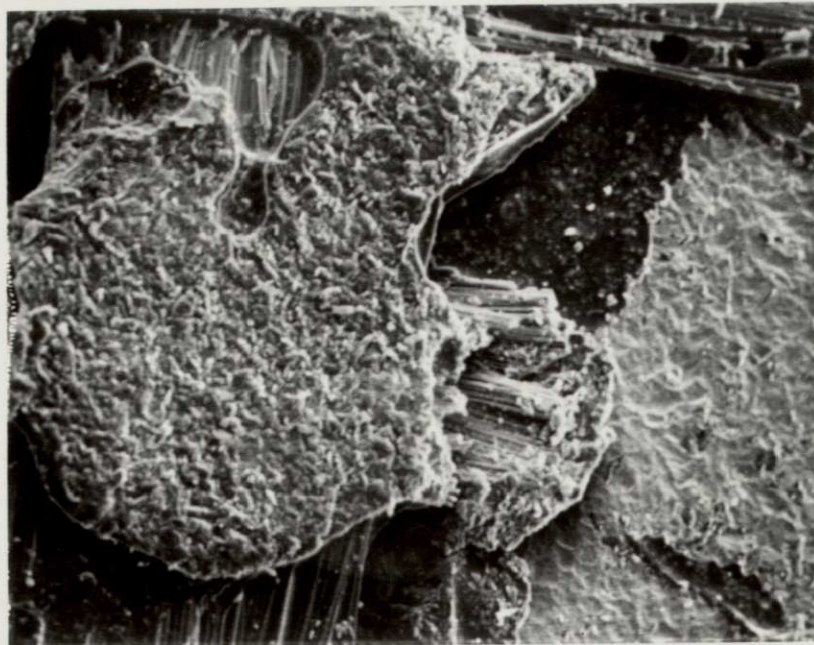
FIGURE 16.

Three magnifications (20X, 100X, 2 @ 500X) of fracture surface of LARC-13 (on scrim cloth)/Ti (phosphate fluoride) tested at room temperature = 1780 psi.



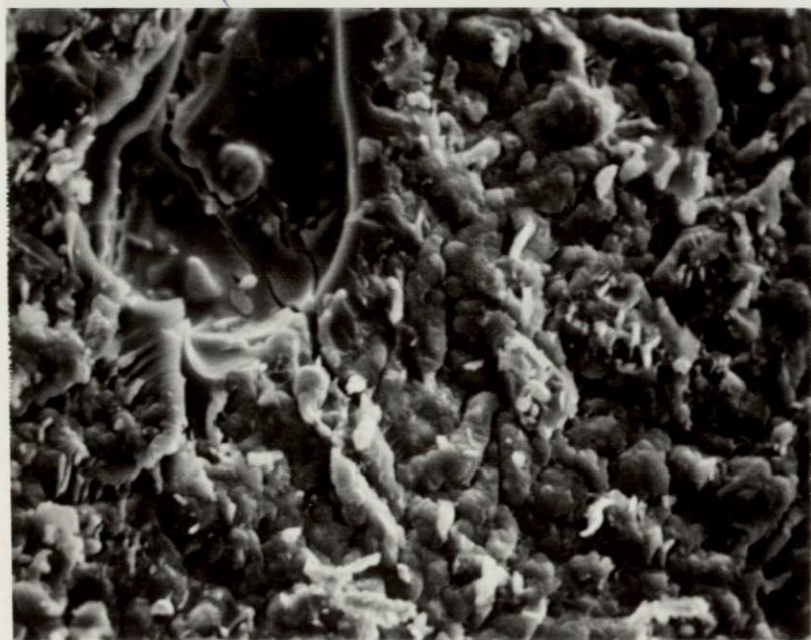


5mm

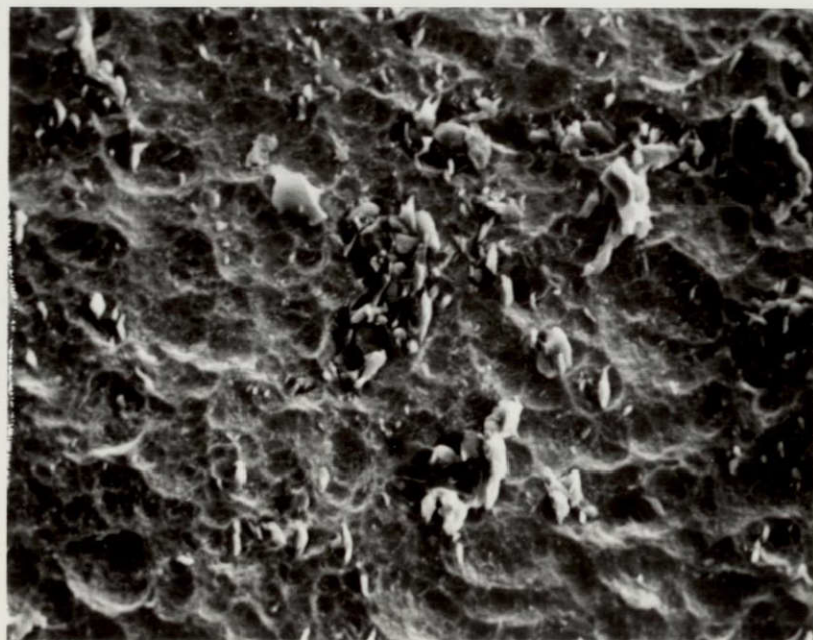


1 mm

not



0.2mm



0.2mm

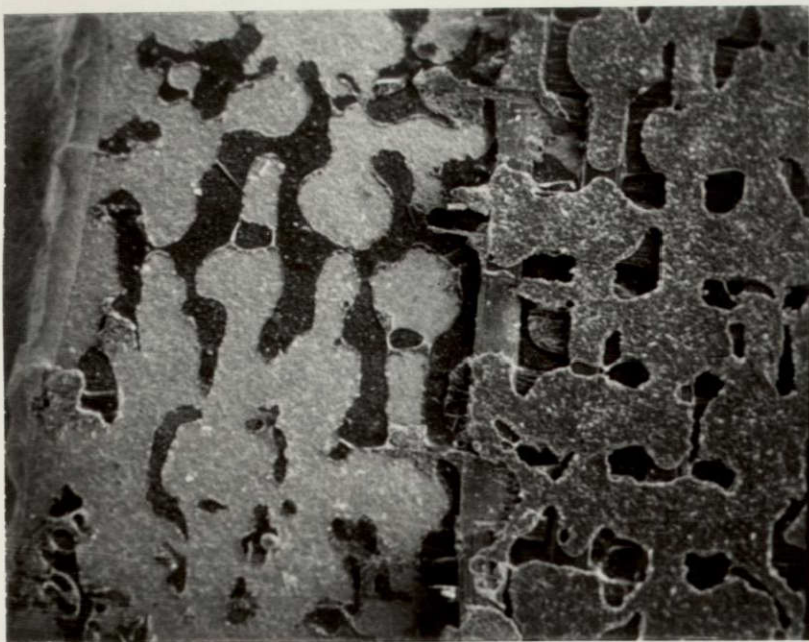




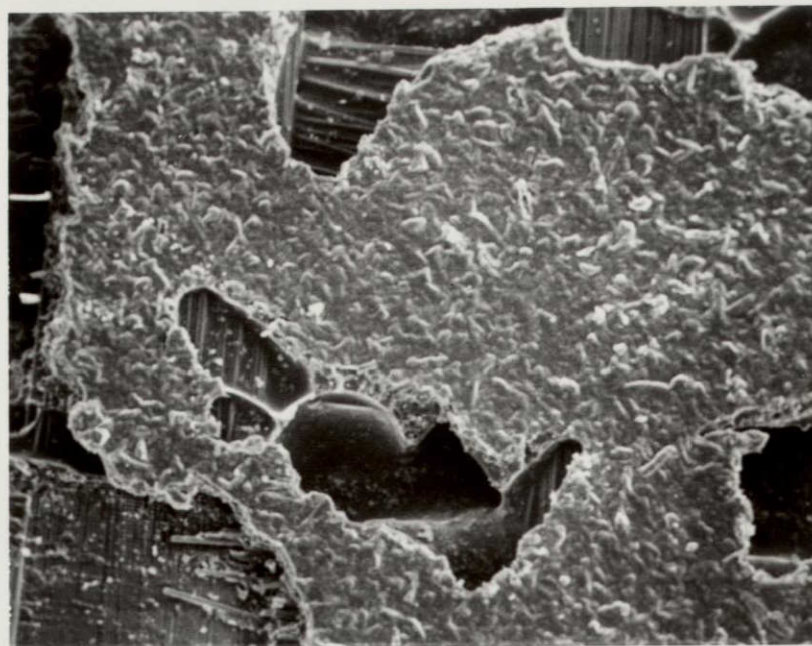
FIGURE 17.

Three magnifications (20X, 100X, 2 @ 500X) of fracture  
surface of LARC-13 (on scrim cloth)/Ti (phosphate fluoride) tested at  
600<sup>0</sup>F = 1200 psi.





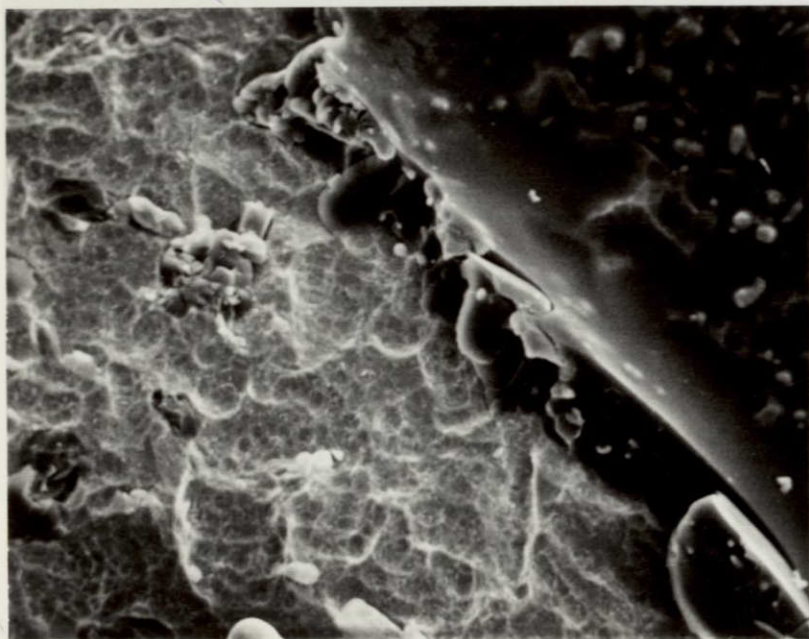
5mm



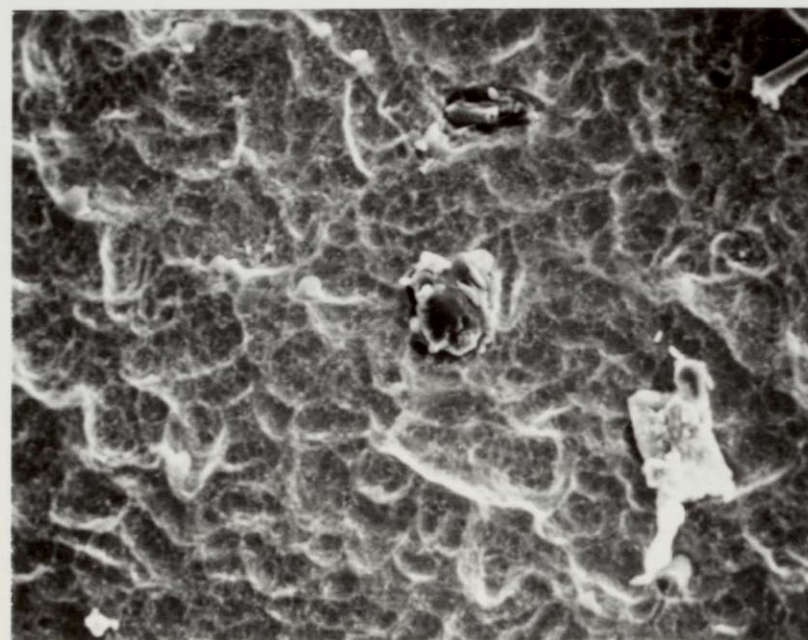
1 mm

SHOULD PLACE IN  
IN PINK QUARTZ

h2-a



0.2 mm



0.2mm

FIGURE 18.

Three magnifications (20X, 100X, 2 @ 500X) of fracture surface of LARC-13 (on scrim cloth)/Ti (phosphate fluoride) sample tested at room temperature after 125 hours aging at 600<sup>o</sup>F = 1940 psi.



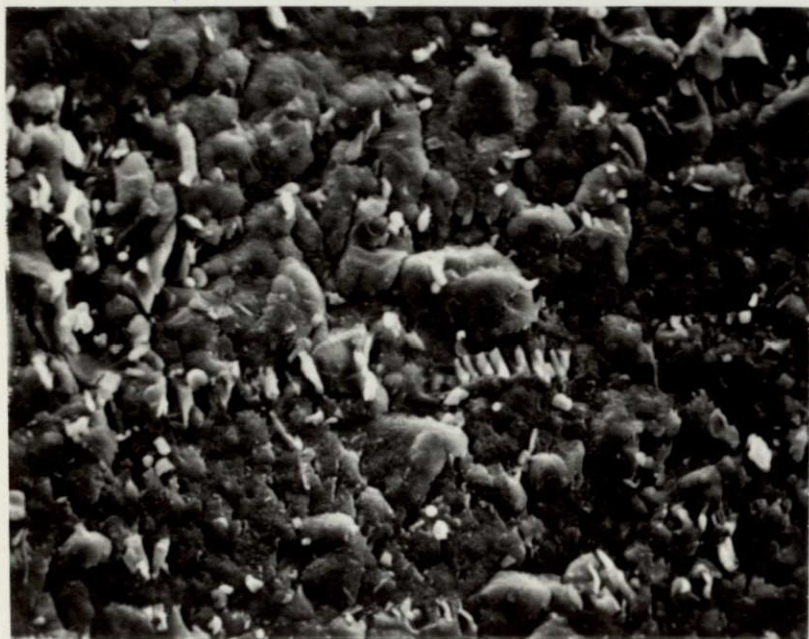


5mm

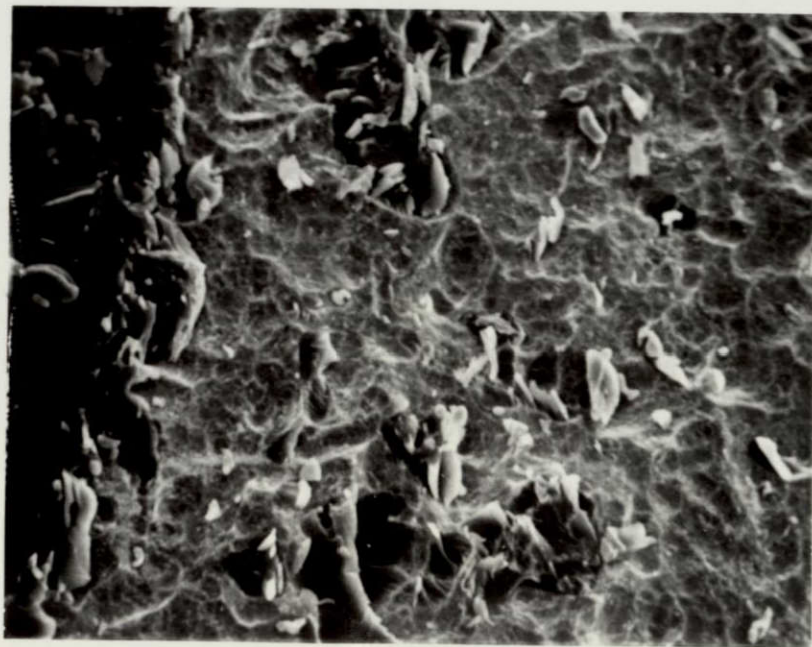


1mm

280



0.2mm



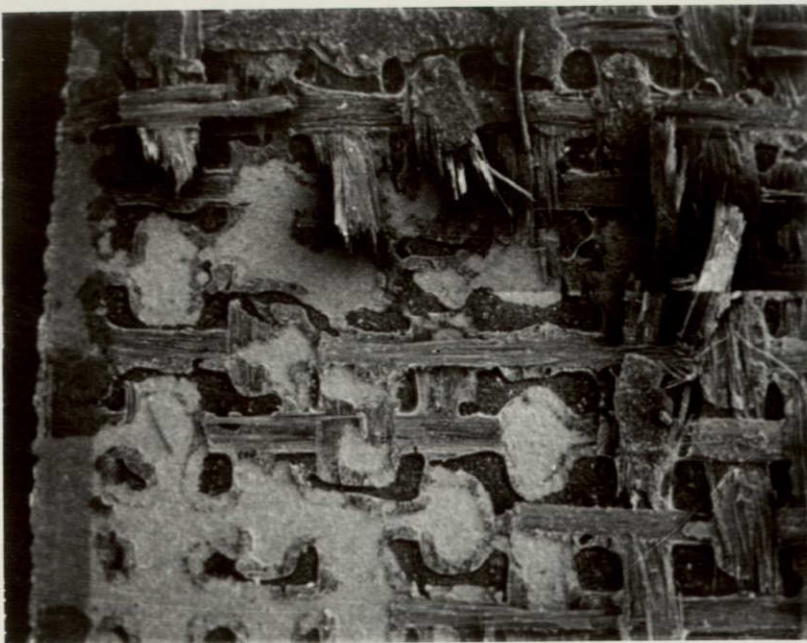
0.2 mm



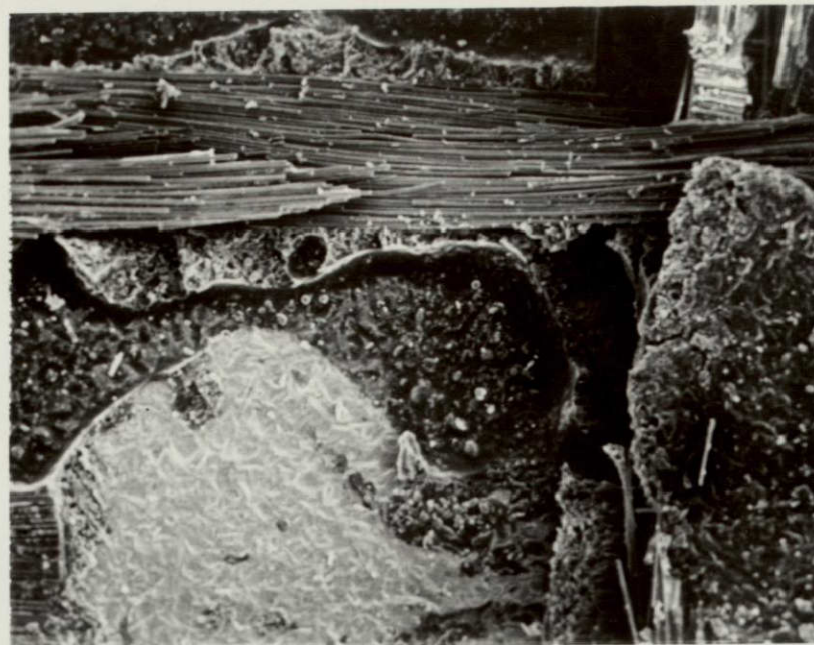
FIGURE 19.

Three magnifications (20X, 100X, 2 @ 500X) of fracture surface of LARC-13 (on scrim cloth)/Ti (phosphate fluoride) sample tested at 600<sup>o</sup>F after 125 hours aging at 600<sup>o</sup>F = 1750 psi.



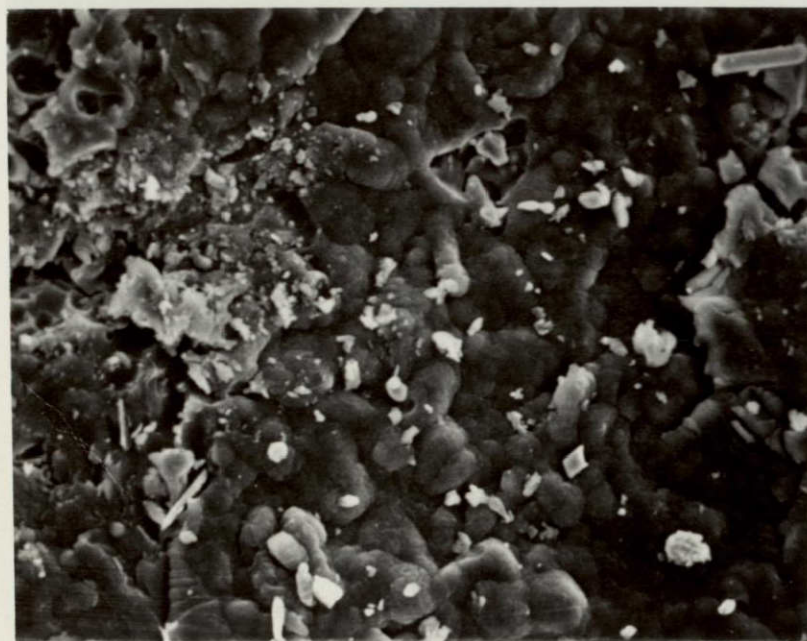


5mm

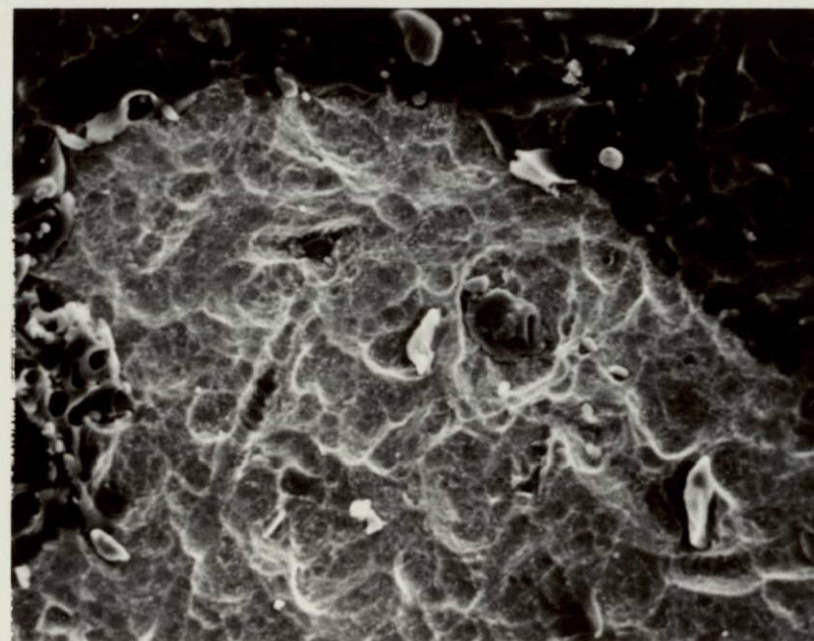


1mm

ORIGINAL PAGE IS  
OF POOR QUALITY



0.2mm



0.2mm

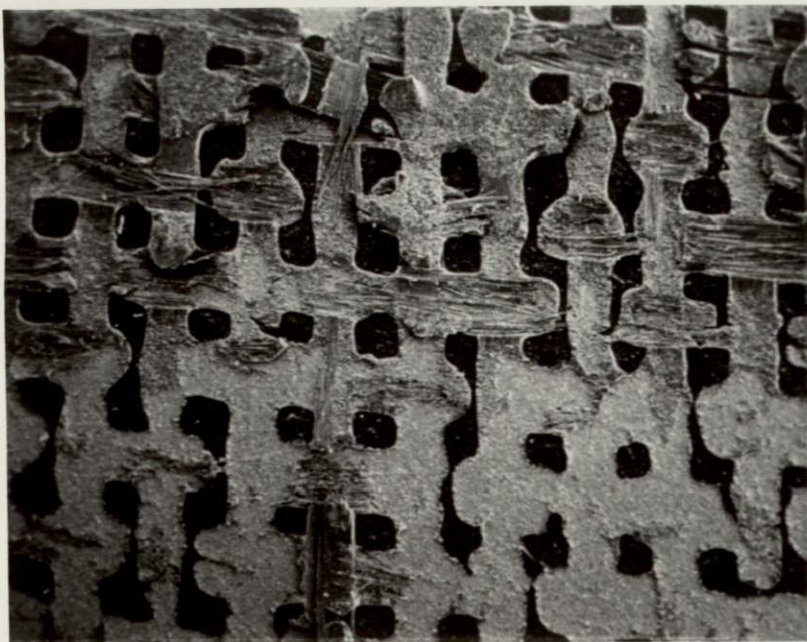
h9a



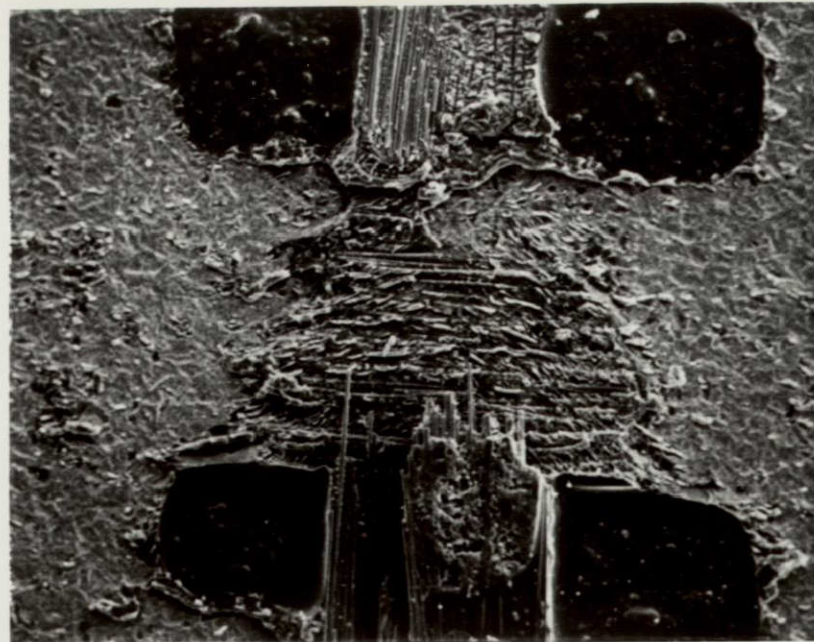
FIGURE 20.

Three magnifications (20X, 100X, 2 @ 500X) of fracture surface of LARC-13 on scrim cloth/Ti (phosphate fluoride) sample tested at room temperature = 3200 psi.





5mm

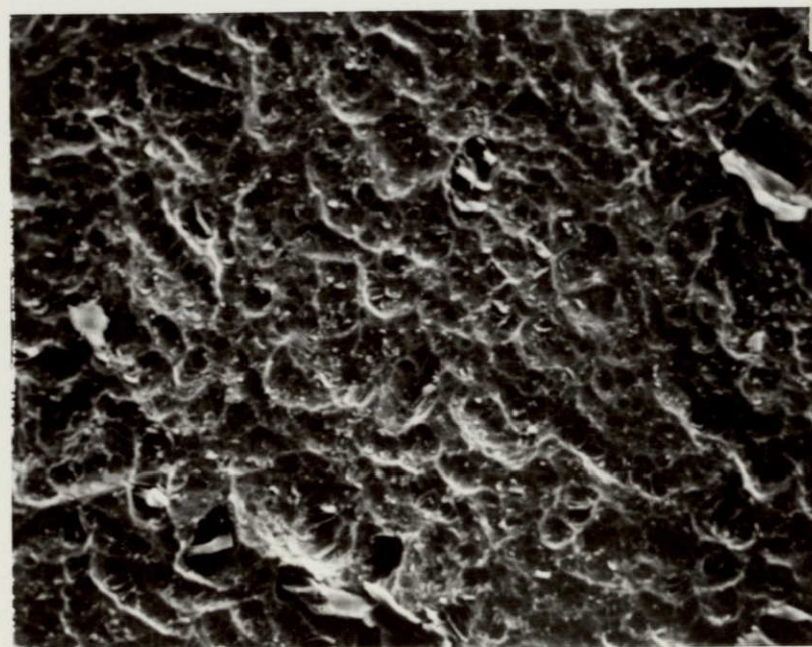


1mm

30a



0.2mm



0.2mm



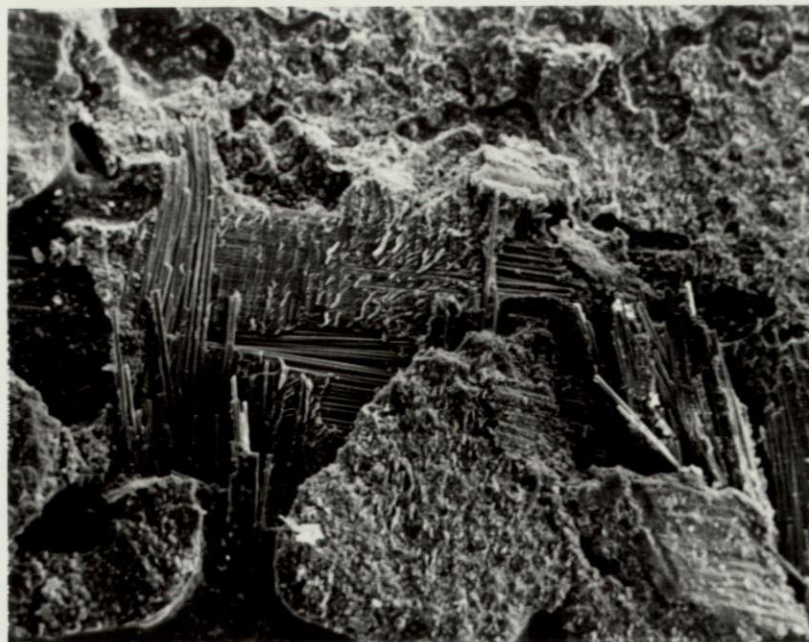
FIGURE 21.

Three magnifications (20X, 100X, 2 @ 500X) of fracture surface of LARC-13 (with 60% Al powder on scrim cloth)/Ti (phosphate fluoride) sample tested at room temperature = 3560 psi.





5mm



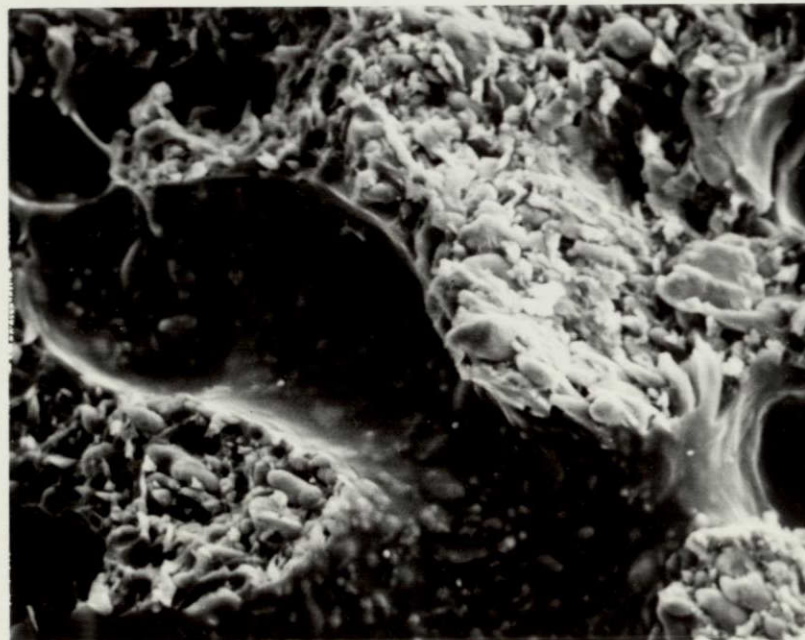
1 mm

ORIGINAL IMAGE  
OF 31-a

31-a



0.2mm



0.2mm



#### IV. Conclusions

1. Special Ti 6-4 samples grit-blasted under various conditions did not show any residual particles. However, these surfaces were all of different microtopography than any previous samples, basically appearing to have been much more heavily worked.

2. New anodized Ti 6-4 samples obtained from Boeing did not show the small nodule structures seen on the previous sample.

3. No significant concentration of extraneous elements was found in a systematic study of composite cross-sections. Infrequent, localized spots were found containing several elements.

4. Interfacial failure dominated the new PPQ samples, and salt "pits" were components on the titanium fracture surfaces.

5. LARC-13 samples also showed considerable interfacial failure, and especially residual voids, indicating low flow during bonding. Increased filler content seemed to reduce the problem.

6. ESCA spectra from a variety of polymers indicated the potential for rapid, "fingerprint" analysis.

#### V. Work Planned

During the remainder of the grant period we expect to complete the analysis of the ESCA spectra of polymers.

Scouting experiments will be conducted in toughening polyimides. A formulation will be developed incorporating fibrillated polytetrafluoroethylene into LARC-2. Experiments will be conducted with known rubber-toughening technology in epoxies as controls. Subsequent to formulation and cure experiments, SEM examination of freeze-fracture specimens will be carried out to observe rubber domains and fracture mechanisms.

Primary effort will be devoted to studies on the durability of surface preparations on Ti 6-4. Surface characterization by SEM/EDAX and ESCA will determine the structure and bonding after each step of the anodized, phosphate/fluoride, Pasa Jell and Turco surface treatments. A new plasma cleaning technique will also be employed to reduce adsorbed contaminants. Accelerated aging will be accomplished by high temperature air exposure, and surface characterization repeated subsequently.



VI. Appendix

ESCA ANALYSIS OF POLYMER STRUCTURE  
AND BONDING, I

by

David W. Dwight, James E. McGrath and  
James P. Wightman

(to be published in Polymer Preprints, Vol. 18, No. 2)

David W. Dwight, James E. McGrath and James P. Wightman  
Department of Chemistry  
Virginia Polytechnic Institute and State University  
Blacksburg, Virginia 24061

X-ray photoelectron spectroscopy (ESCA) provides rapid analysis of diverse polymer samples that can vary from experimental solutions to commercial films. The binding energies and intensities of core-level peaks identify the atoms and functional groups in the sample surface ( $\sim 30 \text{ \AA}$  deep). Unsaturated systems give rise to "shake-up satellite" structures characteristic of local  $\pi$ -bonding. Spectra from a variety of polymers are presented to illustrate some of the potential of ESCA analysis.

ORIGINAL PAGE IS  
OF POOR QUALITY

### INTRODUCTION

Engineering applications for synthetic polymers continue to expand; research and development directed toward defining new properties and processes and elucidating structure-property relationships is critical (1-5). Our previous work emphasized high-performance thermoplastics (6-8) and thermosets (9,10), and characterization of bulk physical properties such as thermal stability, dynamic mechanical behavior, toughness and adhesive-bond strength was of primary importance. ESCA was used mainly for chemical analysis of thin surface layers with composition different from the bulk (11,12).

Clark and co-workers published a series of papers pioneering fundamental ESCA studies of polymers (13). Measurements were made on well characterized, homogeneous polymers and model compounds. The results were correlated with non-empirical, CNDO/2 SCF Molecular Orbital calculations. Their work established that absolute and relative binding energies, and relative peak areas (intensities) are capable of elucidating many important aspects of polymer-surface chemistry.

Another level of information is available in aromatic-containing polymers;  $\pi \rightarrow \pi^*$  transitions give rise to low-intensity "shake-up satellite" structures that are characteristic of the local  $\pi$ -bonding in repeat units (14). Clark, et al., applied this background information to a variety of problems including copolymer composition and structure, structural isomerism, and surface-fluorination kinetics (15).

Other workers have reported primarily fluoropolymer data, since the large chemical shift caused by fluorine substitution facilitates interpretation of the carbon 1s spectra (16). In these systems, ESCA has unique capability to study plasma-polymerized films (17), surface treatments and surface-segregation (11,12).

Included in our current study are commercial, engineering polymers and experimental copolymers from a variety of classes: polyimide, polycarbonate, polyester, polyarylene ether sulfone; polyarylene ether sulfide-sulfone, and polyphenylene oxide. The data show that each polymer system has a distinct ESCA "fingerprint", indicating the potential for rapid, semi-quantitative analysis. Moreover, shake-up satellites may provide new insight into structure and bonding in aromatic-containing polymers.

35



Apparatus

Initial ESCA data were collected on an AEI ES-100 photoelectron spectrometer using an aluminum anode and digital data acquisition. A digital PDP-8e computer/plotter was used to deconvolute and display the spectra. Recently we repeated the experiments on a DuPont 650 photoelectron spectrometer with a magnesium anode and direct display of the spectra on a strip-chart recorder. This system provided analysis of polymer samples in minutes. This is, of course, a significant advantage for routine work even though computer analysis must be added later. We are working on more detailed comparisons but the qualitatively distinctive features of polymers are basically the same in both spectrometers.

Materials and Procedures

Commercial grade films of "Mylar" polyester and "Kapton" polyimide were obtained from DuPont. "Lexan" polycarbonate and "Noryl" polyphenylene oxide were obtained as powders from General Electric. Extruded pellets of polysulfone were obtained from Union Carbide. Both polycarbonate and polysulfone were dissolved in chloroform and examined as cast films. Polyamic acid was cast as a thin film from 15% diglyme and imidization subsequently was accomplished by heating in air for one-hour at 100°, 200° and 300°C. The polythiosulfone (PSF-T) was prepared as described in detail elsewhere (8), and examined as a film cast from chloroform. The monomers bisphenol A and dichlorosulfone were obtained from Union Carbide. Crown Zellerbach supplied the 4,4'-thiodiphenol (Bisphenol T) and 4,4'-sulfonyl diphenol (Bisphenol S).

RESULTS AND DISCUSSION

Interpretation of ESCA spectra of polymers first assumes that effects are localized, and thus characteristic of the repeat unit. The functional constituents are identified by detailed comparison of the spectra with known reference standards or model compounds (monomers). More applications will arise now that the first correlation diagram for carbon 1s levels in polymers as a function of electronic environment has appeared (13). Relatively small chemical-shift effects often result in overlapping of peaks; deconvolution of such spectra aids in identifying the type and amount of functionality. For example, the carbon 1s levels of "Mylar" polyethylene terephthalate are shown in Fig. 1. The four component peaks (dotted lines) add together to exactly match the experimentally determined envelope (solid line). Separation of the ether-, carbonyl-, and aromatic-type carbons and rough estimate of their stoichiometry (1:1:3) are facilitated by deconvolution. However, our AEI digital data acquisition and interactive-computer analysis is relatively time consuming. Figures 2-4 show the results from several polymers and monomers, as obtained in the analog mode with the DuPont spectrometer. For routine analyses the ability to obtain ESCA spectra in minutes may be a significant advantage.

Comparison of Fig. 1 and Fig. 2A shows the same information in the carbon 1s levels as measured by each spectrometer. A shake-up satellite characteristic of  $\pi$ -bonding appears as a high-energy shoulder on the carboxyl peak at higher sensitivity. The oxygen levels are almost resolved into separate peaks for carbonyl- and ether-oxygens, and a shake-up satellite can just be distinguished from the background. Polyphenylene oxide shows relatively intense shake-up satellites in

both carbon and oxygen levels (Fig. 2B). The high-energy (low-intensity) peak in the polycarbonate carbon 1s levels (Fig. 2C) is the combination of shake-up and carbonate peaks. The broad oxygen peak indicates two types of oxygen that differ in environment a little less than the oxygens in "Mylar". One would expect a shake-up satellite but the response was apparently below the signal-to-background ratio. The Bisphenol A model compound spectra in Fig. 2D helps provide confidence in interpretation of spectra of polymers derived from that monomer.

Fig. 3 shows three similar structures that are separated by ESCA. The phenyl-ether link in "Kapton" polyimide (Fig. 3A) results in the broadest carbon and oxygen main peaks, but the carbonyl peak ( $\sim 289\text{eV}$ ) is the narrowest. The potential to follow the thermal cure of polyamic acid to polyimide emerges from Fig. 3B and 3C. The presence of carboxyl groups in the amic acid has a broadening effect on the higher-energy carbon peak and the oxygen levels.

Oxidation of sulfur from thio- to sulfonyl- form produces a distinct chemical shift of about 5 eV, as shown by the model compound spectra in Fig. 4C and 4D. Analysis of polymers for the presence of either of these linkages is straightforward, as illustrated in Fig. 4B. In this case the objective was to obtain an equal number of each. The two oxidation states of oxygen give rise to broad oxygen levels in Fig. 4A and 4B, but curiously do not in 4D.

We are working on more accurate determination of ESCA peak shapes plus deconvolution routines for thorough characterization of structure and bonding in these and other polymer systems.

#### ACKNOWLEDGEMENT

The authors would like to thank NASA and ARO for their support of this research under NSG-1124 and DAAG-76-G0312.

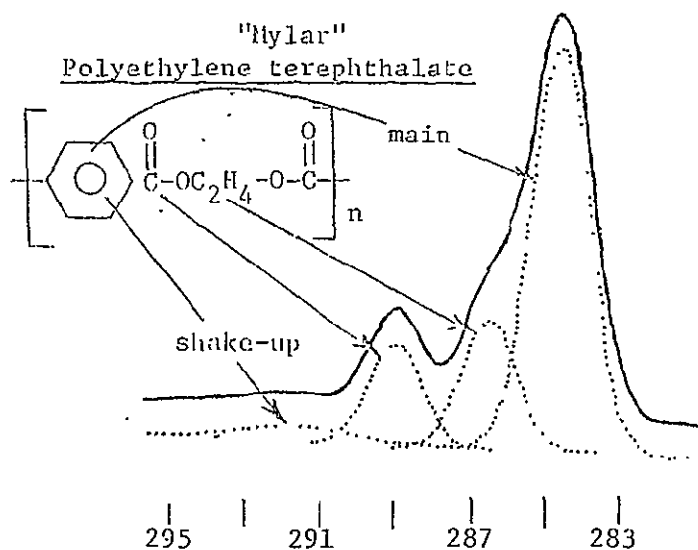
#### REFERENCES

1. "Engineering Design for Plastics", E. Baer editor, S.P.E. Series 104 1964.
2. "Injection Molding of Engineering Thermoplastics", S.P.E. Series 306, June 1977.
3. "The Physics of Glassy Polymers", R. N. Haward Editor, Wiley (1973).
4. "Block Copolymers: Overview and Critical Survey", A. Noshay and J. E. McGrath, Academic Press (1977).
5. "Engineering Plastics and Their Commercial Development", B. F. Foy, editor, ACS No. 96, (1969).
6. M. Matzner, L. M. Robeson, R. Barclay, Jr. and J.E. McGrath, J. Polym. Sci., Symposia, in press (1977).
7. J. E. McGrath, T. C. Ward, E. Shchori and A. J. Wnuk, Polymer Preprints, 18(1), 346 (1977).
8. J. E. McGrath, T. C. Ward, E. Shchori and A. J. Wnuk, Polymer Engineering Science, in press (1977).



9. T. A. Bush, M. E. Counts and J. P. Wightman, in Adhesion Science and Technology, Part A, L.-H. Lee, Ed., Plenum Press, New York, 1975, p. 365.
10. D. W. Dwight, M. E. Counts and J. P. Wightman, in Colloid and Interface Science, Vol. V. III, M. Kerker, Ed., Academic Press, New York, 1976, p. 143.
11. D. W. Dwight and W. M. Riggs, J. Col. and Int. Sci. 47 (3), 650 (1974).
12. D. W. Dwight in Characterization of Metal and Polymer Surfaces, Vol. 2, L.-H. Lee, Ed., Academic Press, 1977, p. 313.
13. D. T. Clark, *ibid.*, p. 5, and references therein.
14. D. T. Clark, D. B. Adams, A. Dilks, J. Peeling and H. R. Thomas, J. Electron Spectrosc. 8, 51 (1976).
15. D. T. Clark in Advances in Polymer Friction and Wear, L.-H. Lee, Ed., Plenum Press, New York, 1975, p. 241.
16. Ginnard, C. R. and Riggs, W. M., Anal. Chem. 44, 1310 (1972).
17. O'Kane, D. F. and Rice, D. W., Polymer Preprints 16, 92 (1975).

Carbon 1s levels



38  
FIGURE I

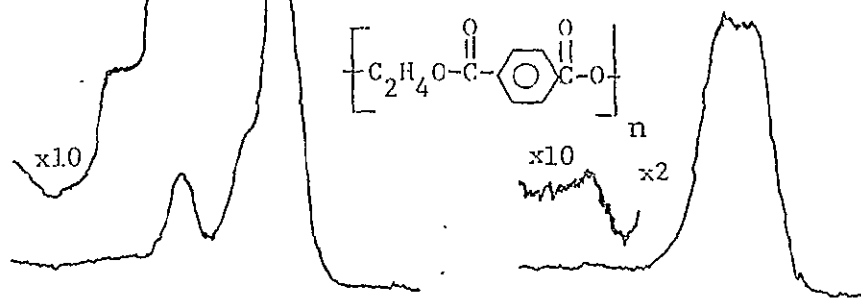
of 97.09  
this line

Carbon 1s  
levels

Oxygen 1s  
levels

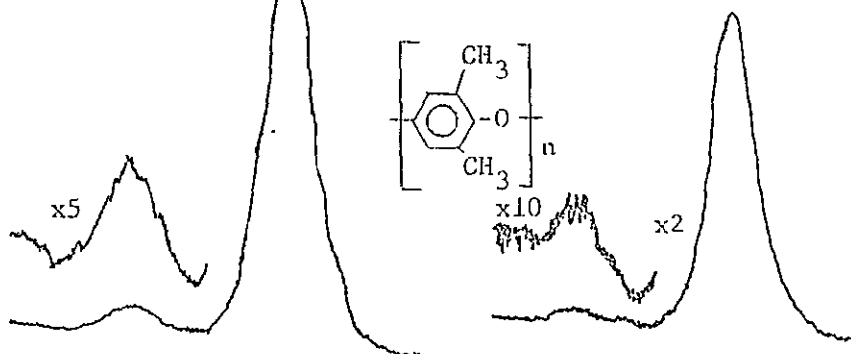
A.

"Mylar" Polyethylene Terephthalate



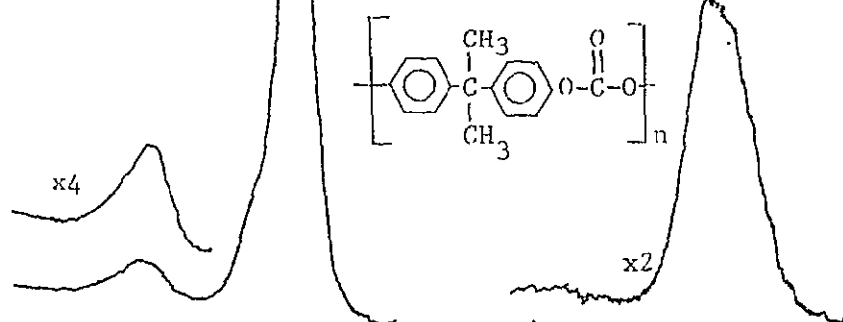
B.

Polyphenylene oxide (PPO)



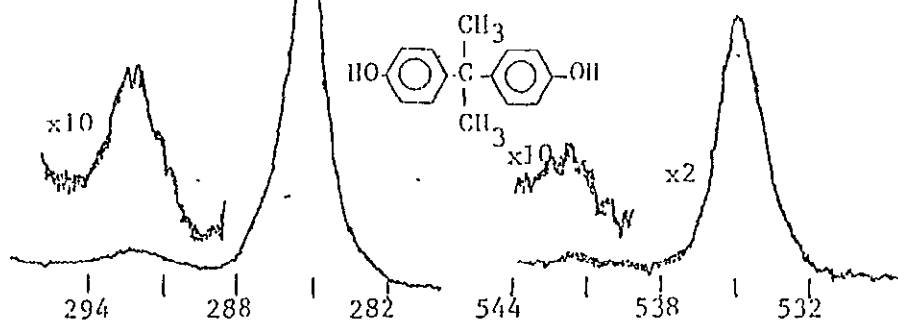
C.

Polycarbonate



D.

Bisphenol A



Binding Energy (eV)

39  
Figure 2



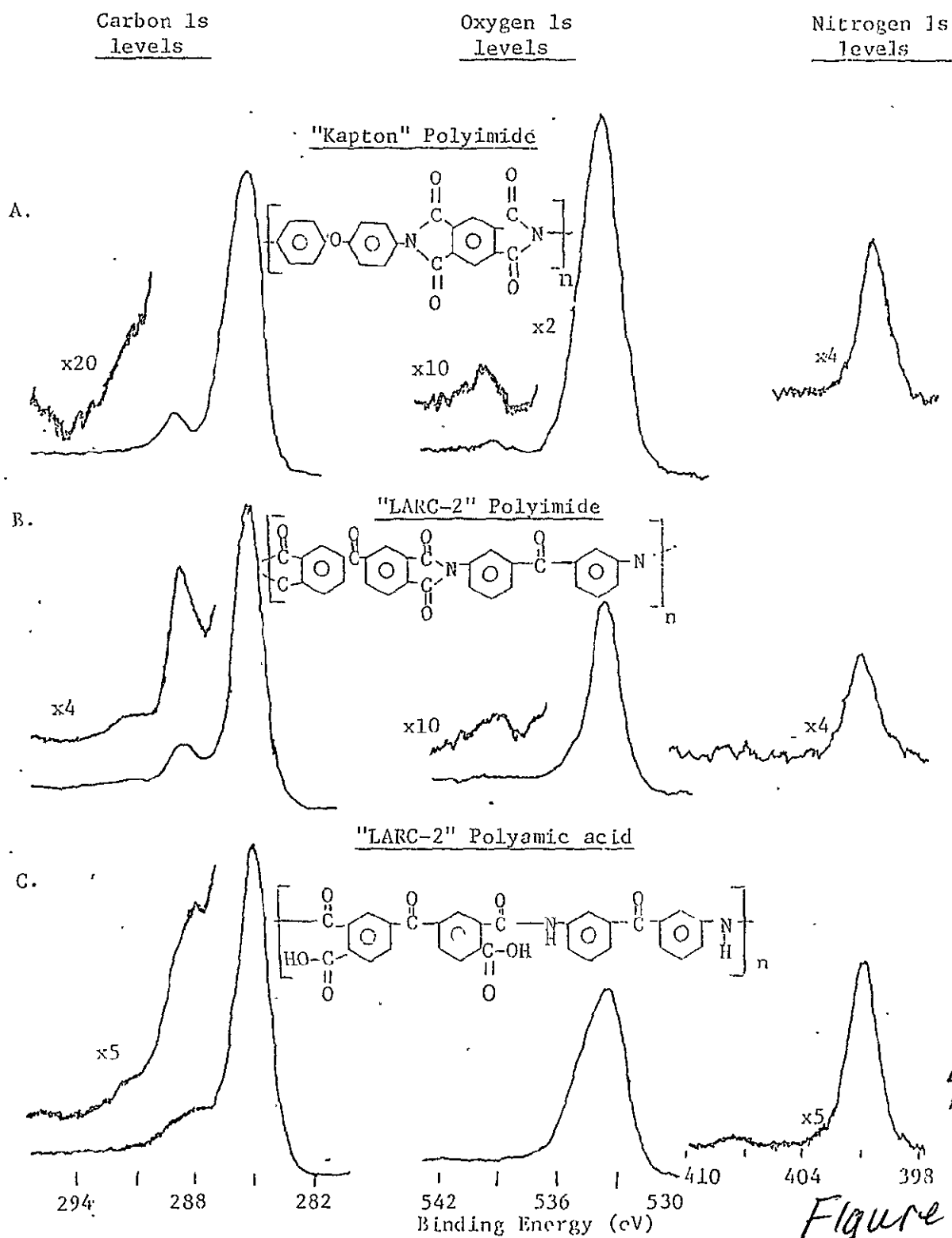


Figure 3

... this line

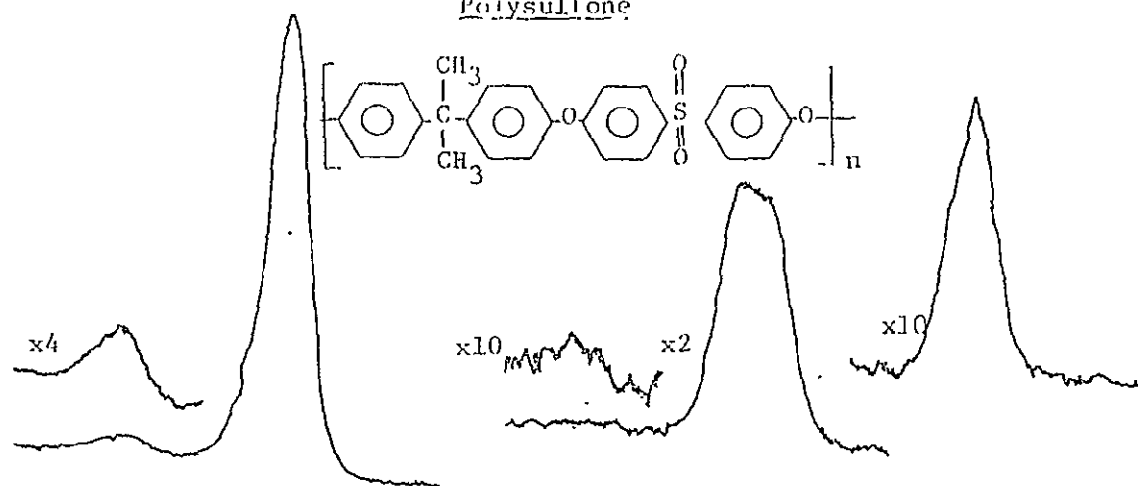
Carbon 1s  
levels

Oxygen 1s  
levels

Sulfur 2p  
levels

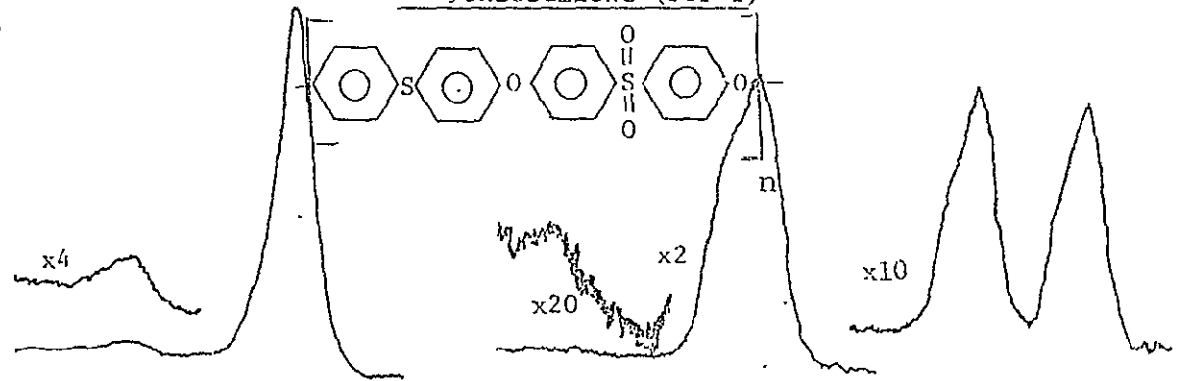
A.

Polysulfone



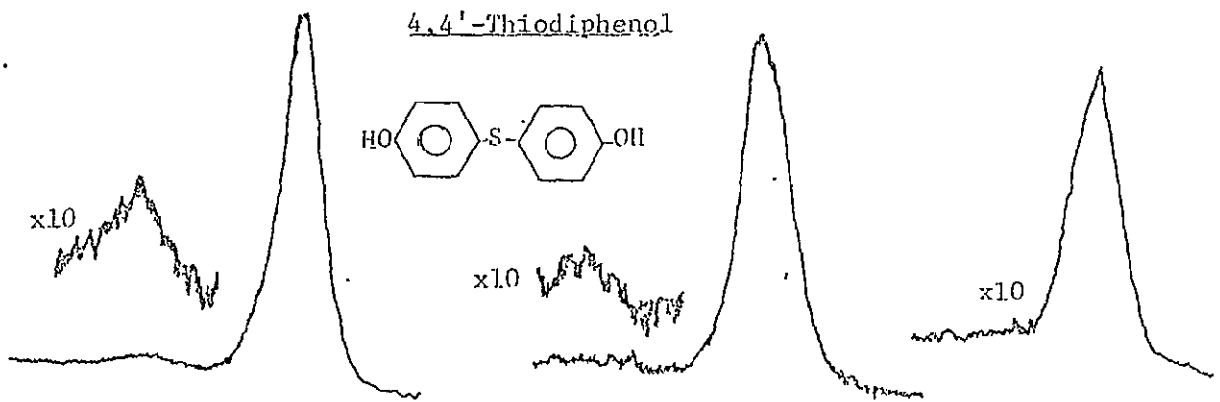
B.

Polythiosulfone (PSF-T)



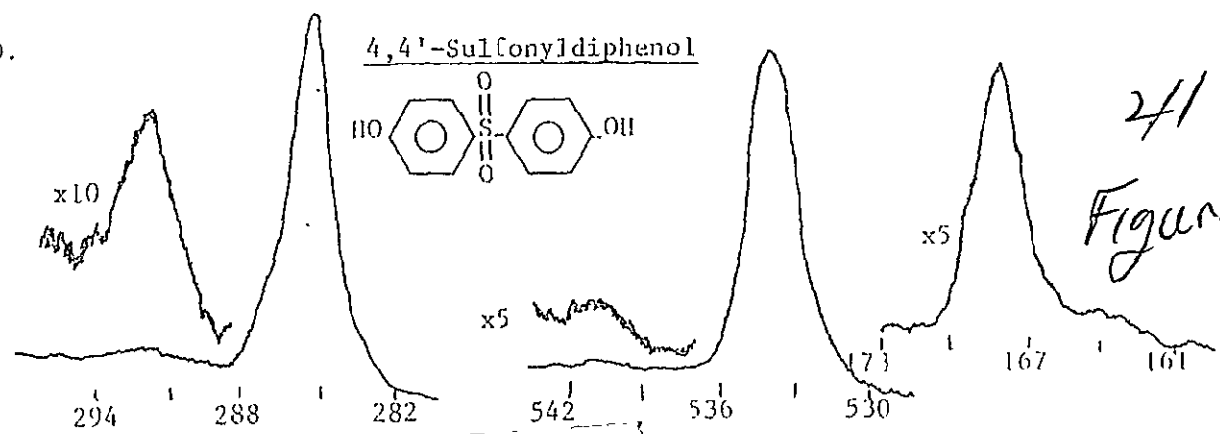
C.

4,4'-Thiodiphenol



D.

4,4'-Sulfonyldiphenol



2/1  
Figure 4

... this line